

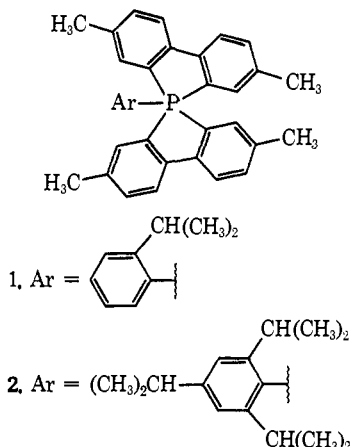
# Pseudorotation in Arylbis(4,4'-dimethyl-2,2'-biphenylene)phosphoranes<sup>1</sup>

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**Abstract:** Examination of the temperature dependence of the proton nmr spectrum of 2-isopropylphenylbis(4,4'-dimethyl-2,2'-biphenylene)phosphorane (**1**) suggests that pseudorotation of this compound does not occur by a simple Berry process but rather by a mechanism involving a square pyramidal intermediate (Scheme I). The permutation of the 4- and 4'-biphenylene sites resulting from this intermediate is the same as that which would result from Berry pseudorotation without an intermediate; however, the presence of an intermediate rationalizes the facile rotation of the 2-isopropylphenyl group around its carbon-phosphorus bond which is observed to be associated with the pseudorotation. Similar although less reliable studies of the spectrum of 2,4,6-triisopropylphenylbis(4,4'-dimethyl-2,2'-biphenylene)phosphorane (**2**) suggest that pseudorotation of this substance takes place by way of an trigonal bipyramidal intermediate or transition state having the triisopropylphenyl group in an axial position. Activation parameters for these pseudorotations are  $\Delta G^\ddagger = 17.8 \pm 0.3$  kcal/mol (56°) for **1** and  $\Delta G^\ddagger = 26.0 \pm 1.2$  kcal/mol (202°) for **2**.

We and others have recently been interested in polytopal rearrangements in derivatives of phosphorus(V).<sup>3-15</sup> In this paper we describe studies of pseudorotation of 2-isopropylphenyl- and 2,4,6-triisopropylphenylbis(4,4'-dimethyl-2,2'-biphenylene)phosphorane (**1** and **2**). These studies deal with a central



problem of this area; does pseudorotation in these

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(2) DAAD (NATO) Postdoctoral Fellow, 1972-1973.

(3) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).

(4) E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 5674 (1972); P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93**, 4701 (1971); J. P. Jesson and P. Meakin, *Accounts Chem. Res.*, **6**, 269 (1973).

(5) M. Eisenhut, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutch, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 5385 (1974), and references cited therein.

(6) G. M. Whitesides and W. M. Bunting, *J. Amer. Chem. Soc.*, **89**, 6801 (1967).

(7) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

(8) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(9) R. R. Holmes, *Accounts Chem. Res.*, **5**, 296 (1972).

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

(11) D. Houalla, R. Wolf, D. Gagnaire, and J. B. Robert, *Chem. Commun.*, 4433 (1969).

(12) J. P. Casey and K. Mislow, *Chem. Commun.*, 1410 (1970).

(13) B. J. Dalton, *J. Chem. Phys.*, **54**, 4745 (1971).

(14) A. H. Cowley and R. W. Braun, *Inorg. Chem.*, **12**, 491 (1973).

(15) P. W. Atkins, *Mol. Phys.*, **13**, 37 (1967); S. P. Mishra and M. C. R. Symons, *Chem. Commun.*, 279 (1974).

pentaarylphosphoranes involve a motion of this type originally suggested by Berry<sup>16</sup> or one of a number of alternative motions?<sup>7,17,18</sup> Compounds **1** and **2** contain two independent stereochemical probes that can be used in conjunction to investigate their pseudorotation. Both are assumed to have trigonal bipyramidal ground state geometries, with the 2,2'-biphenylene groups each bridging one axial and one equatorial position (*vide infra*).<sup>19</sup> The 4- and 4'-methyl groups of these biphenylene moieties are anisochronous at room temperature. The averaging of these chemical shifts observed at high temperatures can be used to determine the rate at which the axial and equatorial ends of the biphenylene moieties interchange. The corresponding temperature dependence of the diastereotopic<sup>20</sup> (by internal comparison) 2-isopropylmethyl signals provides a probe for the rate of interconversion of enantiomers. Comparisons of the rates of axial-equatorial interchange and of enantiomeric interconversion can be used to exclude certain mechanisms for the pseudorotations of **1** and **2**.

## Results and Discussion

Phosphoranes **1** and **2** were prepared following procedures developed by Hellwinkel and coworkers,<sup>21,22</sup> The synthesis of **1** is outlined in Scheme I; that for **2** is analogous.

The spectrum (Figure 1) of the biphenylene methyl protons of the unsymmetrical phosphorane **1** in bromobenzene solution at 33° consists of three lines in the ratio of 1:1:2; four separate biphenylene methyl resonances are clearly resolved in nitrobenzene solution. The isopropyl methyl protons consist of a pair of doublets. On warming, this spectrum collapses

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

(17) J. I. Musher, *J. Amer. Chem. Soc.*, **94**, 5662 (1972).

(18) W. G. Klemperer, *J. Amer. Chem. Soc.*, **94**, 6940 (1972); *Inorg. Chem.*, **11**, 2668 (1972).

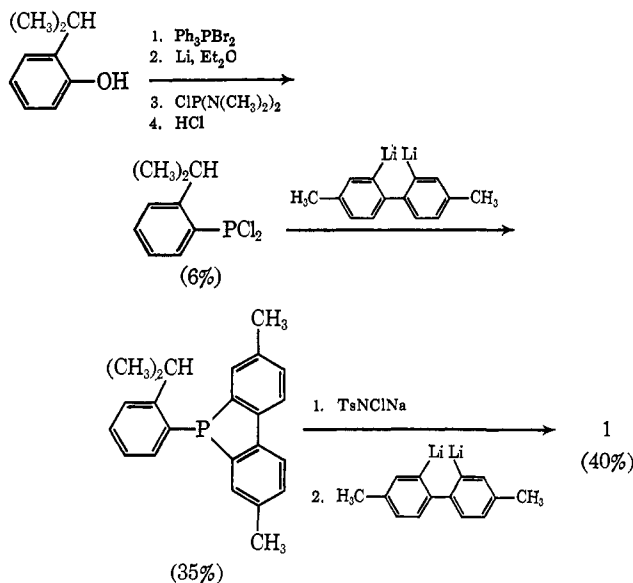
(19) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

(20) M. Raban and K. Mislow, *Top. Stereochem.*, **1**, 1 (1967).

(21) D. Hellwinkel, *Chimica*, **22**, 488 (1968), and references cited therein; D. Hellwinkel and H. J. Wilfinger, *Tetrahedron Lett.*, 3423 (1969).

(22) M. Schlosser, T. Kadibelban, and G. Steinhoff, *Justus Liebig's Ann. Chem.*, **743**, 25 (1971).

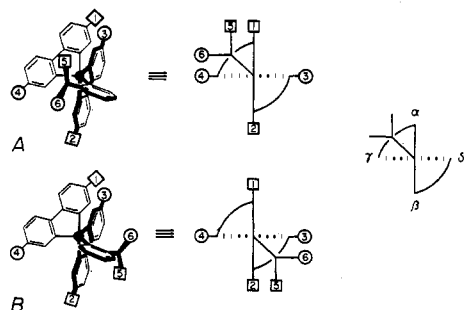
## Scheme I. Synthesis of 1



to a sharp singlet for the biphenylene methyl protons and a sharp doublet for the isopropyl protons.

The magnetic nonequivalence of the four biphenylene methyl groups is consistent with the expected static trigonal bipyramidal structure (e.g., A, Scheme II), with the restriction that rotation of the 2-isopropylphenyl group about the phosphorus-carbon bond ( $A \rightleftharpoons B$ ) is slow on an nmr time scale.<sup>19,23</sup>

## Scheme II



phenyl group about the phosphorus-carbon bond ( $A \rightleftharpoons B$ ) is slow on an nmr time scale.<sup>19,23</sup>

In order to discuss the rearrangement(s) that give rise to the observed temperature dependence of the spectrum of 1, we introduce as shorthand notation to describe the conformations of this substance a simplified projection along the carbon-phosphorus bond of the 2-isopropylphenyl moiety (Scheme II). The numbered circles and squares in A and B in this diagram represent methyl groups and are used to assist in following site permutations that accompany a particular pseudorotation mechanism. The chemical shifts characteristic of each biphenylene methyl group in a frozen conformation are represented by the Greek letters  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ . We assume arbitrarily that the isopropyl group will lie over the face of one of the biphenylene moieties; however, no argument is changed if some other conformation for the 2-isopropylphenyl moiety is preferred. Using the procedures described by Klemperer,<sup>18,24</sup> the possible differentiable reactions

(23) General reviews of structural work related to five-coordinate compounds are B. F. Hoskins and F. D. Whillans, *Coord. Chem. Rev.*, **9**, 365 (1973), and J. S. Wood, *Progr. Inorg. Chem.*, **16**, 227 (1972); R. R. Holmes, *J. Amer. Chem. Soc.*, **96**, 4143 (1974).

(24) We wish to thank Professor Walter Klemperer for his help in constructing Table I.

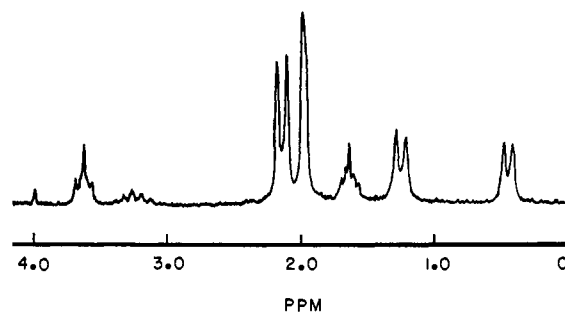


Figure 1. Nmr spectrum (100 MHz) of 2-isopropylphenylbis(4,4'-dimethyl-2,2'-biphenylene)phosphorane (1) in bromobenzene-tetrachloroethane solution (ca. 70:30) at 33°. The aromatic region of 1 is not shown. Resonances at  $\delta$  1.7 and 3.7 are due to tetrahydrofuran of solvation. The small peak at  $\delta$  4.0 is an impurity.

for 1 are listed (Table I); 3 and 4 are reference isomers

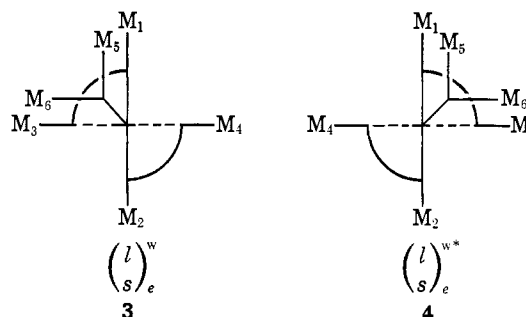


Table I. Differentiable Permutational Isomerization Reactions for 1 Based on Reference Isomers 3 and 4

Reaction <sup>a</sup>	Resonances averaged <sup>b</sup>
$h_1^{ww} = (1)(3)(24)(5)(6)^{ww}$	$M_2 + M_4$
$h_2^{ww} = (13)(2)(4)(5)(6)^{ww}$	$M_1 + M_3$
$h_3^{ww} = (13)(24)(5)(6)^{ww}$	$M_1 + M_3; M_2 + M_4$
$h_4^{ww} = (12)(34)(5)(6)^{ww}$	$M_1 + M_2; M_3 + M_4$
$h_5^{ww} = (14)(23)(5)(6)^{ww}$	$M_1 + M_4; M_2 + M_3$
$h_6^{ww} = (1234)(5)(6)^{ww}$ <sup>c</sup>	$M_1 + M_2 + M_3 + M_4$
$h_7^{ww} = (1432)(5)(6)^{ww}$ <sup>c</sup>	$M_1 + M_2 + M_3 + M_4$
$h_8^{ww*} = (1)(2)(3)(4)(56)^{ww*}$	$M_5 + M_6$
$h_9^{ww*} = (1)(3)(24)(56)^{ww*}$	$M_2 + M_4; M_5 + M_6$
$h_{10}^{ww*} = (13)(24)(56)^{ww*}$	$M_1 + M_3; M_2 + M_4;$ $M_5 + M_6$
$h_{11}^{ww*} = (12)(34)(56)^{ww*}$	$M_1 + M_2; M_3 + M_4;$ $M_5 + M_6$
$h_{12}^{ww*} = (14)(23)(56)^{ww*}$	$M_1 + M_4; M_2 + M_3;$ $M_5 + M_6$
$h_{13}^{ww*} = (1234)(56)^{ww*}$ <sup>c</sup>	$M_1 + M_2 + M_3 + M_4;$ $M_5 + M_6$
$h_{14}^{ww*} = (1432)(56)^{ww*}$ <sup>c</sup>	$M_1 + M_2 + M_3 + M_4;$ $M_5 + M_6$
Observed	$M_1 + M_2 + M_3 + M_4;$ $M_5 + M_6$

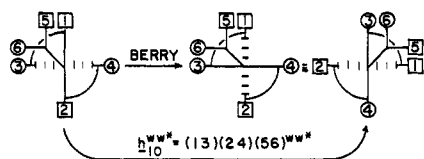
<sup>a</sup> For each isomerization reaction represented by  $h_i^{ww}$ , there is a corresponding  $h_i^{ww*}$  and for each  $h_i^{ww*}$  a corresponding  $h_i^{ww}$ .

<sup>b</sup> Here, for example,  $M_1 + M_3; M_2 + M_4$  means that the resonances of methyls 1 and 3 will coalesce to a single line and the resonances of methyls 2 and 4 will coalesce to a separate line, which may or may not overlap the first. <sup>c</sup> These bracketed permutations must be considered together, since they are not individually microscopically reversible.

for the two enantiomeric series. This table also lists the resonances that would coalesce as a result of the averaging of chemical shifts by these reactions.

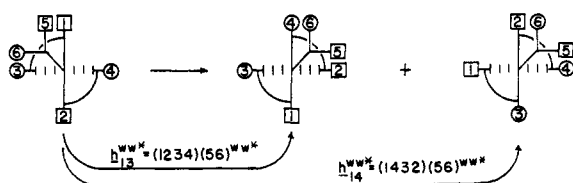
In total there are 12 differentiable permutational isomerization reactions, since the pairs of reactions represented by  $h_6^{ww}$  and  $h_7^{ww}$  and by  $h_{13}^{ww*}$  and  $h_{14}^{ww*}$

are the microscopic reverse of one another and must be considered together. *The two, qualitative, experimental observations that the four biphenylene methyl resonances coalesce to a single averaged line at high temperature and that the isopropyl methyl resonance collapse to a doublet, lead to the remarkable conclusion that all of these reactions, with the exception of those represented by  $h_{13}^{ww*} + h_{14}^{ww*}$ , can be ruled out as being solely responsible for the temperature dependence of the spectrum.* Any process that leaves the chirality at phosphorus unchanged ( $h_{1-7}^{ww}$ ) can be discarded, since such a process would leave the isopropyl signals unchanged. Of the remaining processes,  $h_{8-12}^{ww*}$  would yield two or more lines for the biphenylene methyl resonances at the high temperature limit. Note particularly that a Berry pseudorotation in which the 2-isopropylphenyl group remains above the same biphenylene moiety ( $h_{10}^{ww*}$ ) throughout the course of



the pseudorotation is not compatible with the observed spectral changes.

The combined permutational isomerization  $h_{13}^{ww*} + h_{14}^{ww*}$  predicts qualitatively the observed co-

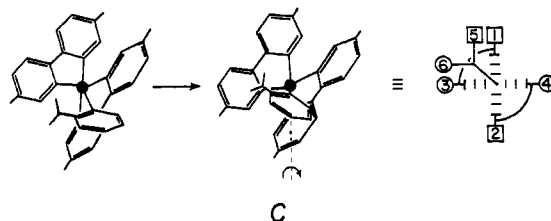


alescence of the four biphenylene methyl resonances and is microscopically reversible. However, it is not immediately evident what physically reasonable mechanism, if any, might yield this permutation. It is particularly difficult to conceive of a concerted process that would transfer the 2-isopropylphenyl moiety from the face of one biphenyl moiety to the face of the second on each pseudorotation event.

Combinations of the permutational isomerizations of Table I are capable of averaging the four lines due to the biphenylene methyl groups and the resonances of the diastereotopic isopropyl methyl groups. However, the number of possible combinations is large, and their enumeration is not likely to be particularly helpful in suggesting possible mechanisms for the pseudorotation of **1**. Since no single, physically acceptable, concerted mechanism compatible with the assumption that **1** exists exclusively in a trigonal bipyramidal structure with the 2-isopropylaryl group equatorial seems able to rationalize the spectral line shapes, we have examined the consequence of plausible nonconcerted mechanisms. The two simplest mechanisms generating significant intermediates would be (1) a Berry pseudorotation, maintaining the 2-isopropylphenyl group as pivot, leading to a square pyramidal intermediate whose lifetime was great enough to allow rotation around the phosphorus-carbon bond leading to the 2-isopropyl group, and (2) a Berry pseudorotation in which a carbon-phosphorus bond of one of the biphenylene moieties served as pivot, leading to an

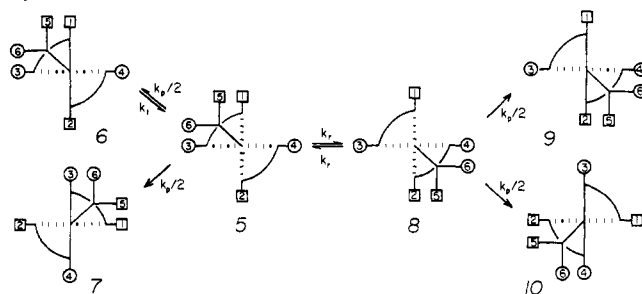
intermediate trigonal bipyramid in which the 2-isopropylphenyl group was axial. This intermediate might also have a lifetime long enough to allow rotation around the phosphorus-2-isopropylphenyl bond. Intermediates of both types have been postulated previously in related studies.<sup>11,21</sup>

**Mechanisms Involving a Square Pyramidal Intermediate.** The Berry mechanism for pseudorotation is incompatible with the temperature dependence of the spectrum of **1** because it provides no mechanism for rotation of the 2-isopropylphenyl moiety from a position covering the face of one biphenylene ring to one covering the face of the second. A plausible modification of this mechanism would invoke a square pyramidal intermediate along the pseudorotation coordinate and permit rotation of the 2-isopropylphenyl moiety in this intermediate. The hypothetical square pyramidal intermediate (C) would be represented by an obvious



modification of the projection formula used earlier. A kinetic scheme based on an intermediate of this structure that is capable of accounting for magnetization transfer among all four of the biphenylene methyl groups requires only three rate constants: that for formation of the square pyramidal conformer from its trigonal bipyramidal precursor,  $k_t$ , that for rotation of the 2-isopropylphenyl group around the carbon-phosphorus bond,  $k_r$ , and that for return of square pyramidal to trigonal bipyramidal geometry,  $k_p$  (Scheme III).

**Scheme III.** Pseudorotation Proceeding through a Square Pyramidal Intermediate



If one assumes that the sample is initially in conformation **6**, suddenly undergoes a transition to **5**, and subsequently partitions among **6**, **7**, **9**, and **10**, it is possible to show that the **K** matrix in eq 1 describes

$$\mathbf{K}_{\text{III}} = \begin{matrix} & \begin{matrix} \textcircled{1} & \textcircled{2} & \textcircled{3} & \textcircled{4} & \textcircled{5} & \textcircled{6} \end{matrix} \\ \begin{matrix} \textcircled{1} \\ \textcircled{2} \\ \textcircled{3} \\ \textcircled{4} \\ \textcircled{5} \\ \textcircled{6} \end{matrix} & \begin{bmatrix} -a & b & c & b & & \\ b & -a & b & c & & \\ c & b & -a & b & & \\ b & c & b & -a & & \\ & & & & -k_t/2 & k_t/2 \\ & & & & k_t/2 & -k_t/2 \end{bmatrix} \end{matrix} \quad (1)$$

$$\begin{aligned} a &= k_t(3k_r + k_p)/(4k_r + 2k_p) \\ b &= k_t k_r/(4k_r + 2k_p) \\ c &= k_t(k_r + k_p)/(4k_r + 2k_p) \end{aligned}$$

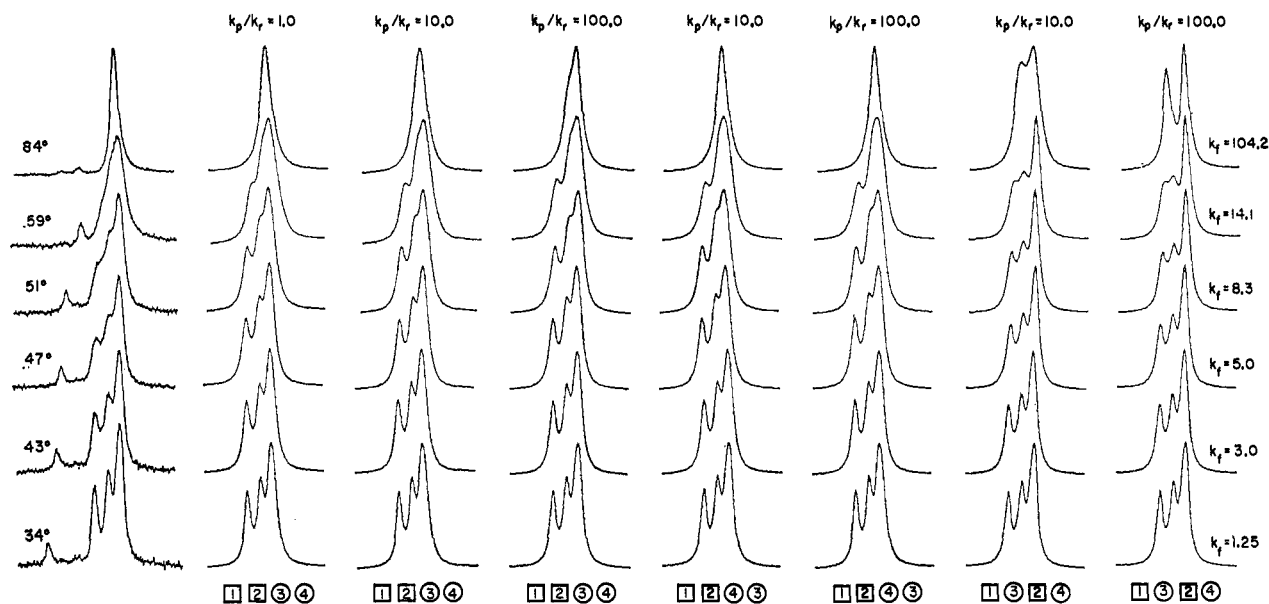
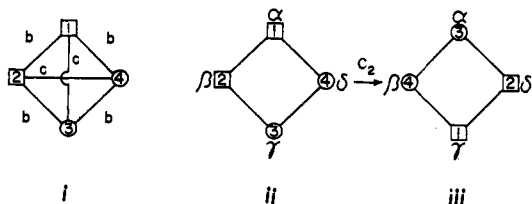


Figure 2. Spectra calculated assuming Scheme III.

the transfer of magnetization among the biphenylene methyl groups 1, 2, 3, and 4 and among the 2-isopropyl methyl groups 5 and 6.<sup>25</sup> Before this equation can be used in its most general form to simulate the line shapes of 1, specific frequencies from the static experimental spectrum must be assigned to the methyl groups. This assignment presents no difficulties for the isopropyl methyl groups, since the spectrum is invariant to the assigned chosen. Assignment of the frequencies of the biphenylene methyl multiplet to particular methyl groups is more complicated. In principal, there are  $4! = 24$  ways in which these assignments might be made in spectra of 1 in nitrobenzene solution, in which all four resonances are distinct, or 12 ways in bromobenzene solution, in which two resonances coincide. Testing even 12 distinct assignments for their ability to reproduce line shapes is clearly an impractical enterprise. Fortunately, the symmetry of that part of  $K_{III}$  that describes transfer of magnetization among the biphenylene methyl groups is sufficiently high that only three distinct types of assignments need be considered in instances in which four lines are resolved.<sup>26</sup> These classes of assignments are indicated schematically in Scheme IV; assignments I and II clearly lead to identical line shapes in the intermedi-

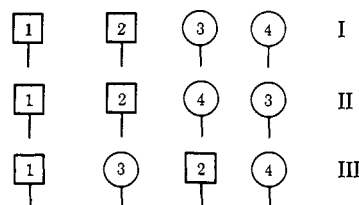
(25) This  $K$  matrix is derived in supplementary material. See paragraph at end of the paper.

(26) This symmetry is most easily recognized by construction of a diagram outlining the magnetization transfer between methyl groups required by eq 1 (i). This diagram has  $D_4$  symmetry. Hence,



for any arbitrary assignment of chemical shifts to the four methyl groups, all of the assignments generated by applying the covering operations of the  $D_4$  point group to an initial assignment will lead to indistinguishable spectra in any exchange process described by eq 1. For example, the assignments indicated by ii and iii are spectroscopically indistinguishable.

Scheme IV. Distinguishable Assignments of Resonances of the Biphenylene Methyl Region of 1 to Particular Methyl Groups<sup>a</sup>



<sup>a</sup> In the experimental spectrum of Figure 1, the two lines at highest field are not resolved.

ate exchange region when the resonances of the 3 and 4 methyl groups are superimposed.

In order to establish which of the assignments outlined in Scheme IV leads to calculated spectra in best agreement with experimental spectra, assuming the mechanism outlined in Scheme III and  $K_{III}$ , we have calculated spectra for the biphenylene methyl region of 1 for a range of values of the parameters  $b$  and  $k_p/k_r$ .<sup>27,28</sup> The useful conclusion that emerges from comparison of these line shapes with the experimental spectra (Figure 2) is that any of the three distinguishable chemical shift assignments (Scheme IV) leads to indistinguishable calculated line shapes for  $k_p/k_r \leq 1.0$ , and all of these calculated line shapes are in good agreement with the experimental spectra. The calculated line shapes for any of these assignments at values of  $k_p/k_r \leq 1.0$  are not significantly different from those reproduced in Figure 2 for assignment I at  $k_p/k_r = 1.0$  and are not reproduced here. Thus, any of the possible chemical shift assignments fits the observed spectra, provided that  $k_p/k_r \leq 1$ . None of the chemical shift assignments gives satisfactory agreement between calculated and theoretical spectra for  $k_p/k_r \geq 10$ , al-

(27) The block of eq 1 describing the biphenylene methyl region can be conveniently rewritten for this purpose by dividing all of its elements by  $b$ , since  $c/b = 1 + (k_p/k_r)$  and  $a/b = 3 + (k_p/k_r)$ .

(28) Calculations were carried out using unexceptional procedures: cf. C. S. Johnson, Jr., *Advan. Magn. Resonance*, 1, 33 (1965); G. Binsch, *Top. Stereochem.*, 3, 97 (1968); I. O. Sutherland, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, 4, 71 (1971), and references cited in each. The program used has been described: J. K. Krieger, J. M. Deutch, and G. M. Whitesides, *Inorg. Chem.*, 12, 1535 (1973).

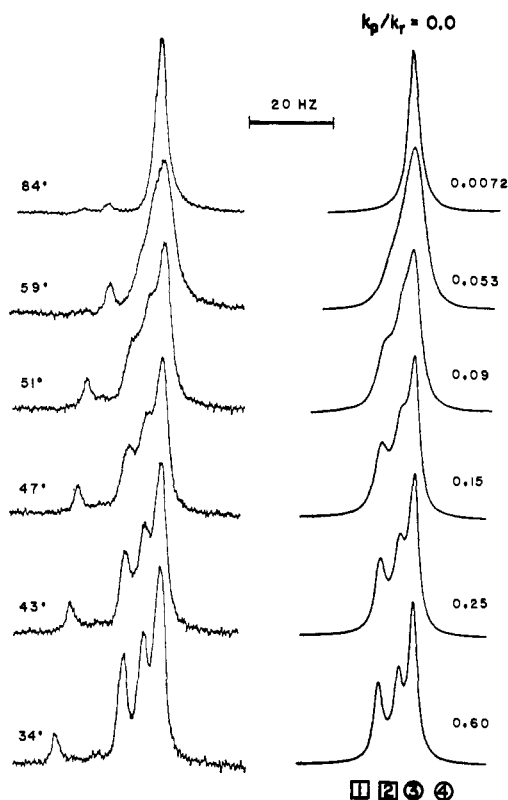


Figure 3. The matched experimental ( $T$ , °C) and calculated ( $\tau$ , sec) spectra for the biphenylene methyl resonances of **1**.

though the agreement is closer for assignment I than for assignments II or III (Figure 2).<sup>29</sup>

Since any value of  $k_p/k_r \leq 1$  gives equally satisfactory agreement between calculated and experimental spectra, we have arbitrarily simplified further calculations by assuming that  $k_r \gg k_p$ . Neglecting  $k_p$  in eq 1,  $a = (3/4)k_t$  and  $b = c = (1/4)k_t$ . This form of the **K** matrix was used in fitting calculated spectra of both the biphenylene and isopropyl methyl regions (Figures 2 and 3). In calculating these spectra, the chemical shift differences between the methyl peaks were assumed to be temperature independent. This assumption was tested by examining these chemical shifts over 50° below the slow exchange region (see the Experimental Section).

The only important point to consider concerning these spectra is the precision with which they permit the magnitude of  $k_t$  to be estimated at any particular temperature. This precision is of concern in discussions of mechanisms for pseudorotation of **1** that are alternatives to that outlined in Scheme III. We believe that the sensitivity of the calculated line shapes to  $k_t$  illustrated by Figures 2 and 4, is sufficient that the "best" values of  $k_t$  for the biphenyl methyls and the "best" values of  $k_t$  for the isopropyl methyls can, in fact, be determined relative to one another at a common temperature to

(29) Professor D. Hellwinkel has interpreted nmr studies of compounds similar to **1** and **2** to support pseudorotation schemes of the type  $vi \rightleftharpoons iv \rightleftharpoons v$ . This scheme is compatible with our kinetic results so long as  $k = k'$ ; cf. D. Hellwinkel, W. Lindner, and H. J. Wilfinger, *Chem. Ber.*, submitted for publication.

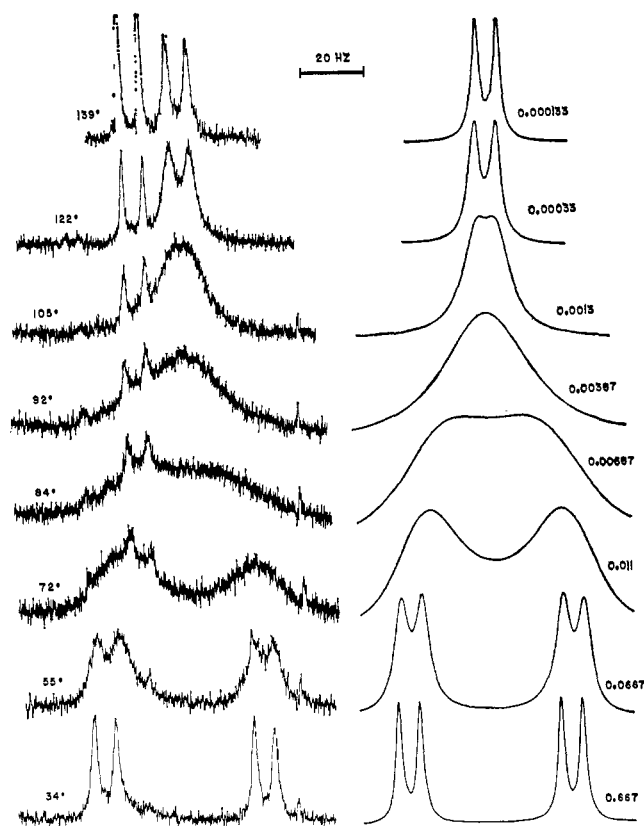
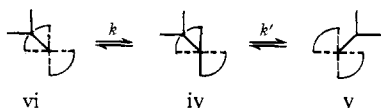


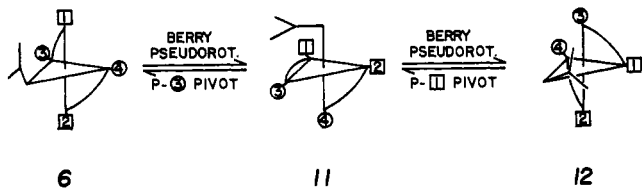
Figure 4. Matched experimental ( $T$ , °C) and calculated ( $\tau$ , sec) spectra for the isopropyl methyl resonances of **1**. The extraneous peaks that increase in intensity at high temperatures are due to an unidentified thermal decomposition product.

better than a factor of 2. We base this belief on the Arrhenius plot constructed from these data. Certainly, over the particular temperature regions in which the line shapes change most rapidly, experimental and calculated spectra can be fitted with error of appreciably less than 100%. Unfortunately, these regions of highest sensitivity do not overlap for the biphenylene methyl resonances and the isopropyl methyl resonances, and it is not possible to make relative comparisons for these resonances at the same temperature. Instead, we have plotted the data from both sets of methyl groups on the same Arrhenius plot, and drawn independent least-squares lines through each set (Figure 5). These lines have approximately parallel slopes, displaced by an average value over the region of overlap of approximately  $0.173 = \log 1.49$ .

In summary, the important conclusions from this section for understanding the pseudorotation of **1** are that Scheme III is compatible with the experimental spectra data, with the proviso that  $k_r > k_p$ . A number of simpler schemes, including a concerted Berry pseudorotation (represented by  $h_{10}^{w*w}$ ), are not. Further, within the context of the mechanism outlined by Scheme III, it appears that the rate of axial-equatorial interchange of biphenylene methyl groups differs by less than a factor of 2 different from the rate of inversion of chirality at phosphorus.

**Mechanisms Involving a Biphenylene Carbon Center as the Pivot of a Berry Pseudorotation.** Although the foregoing discussion establishes that Scheme III is compatible with the experimental data for pseudorotation of **1**, it does not establish that this scheme is uniquely

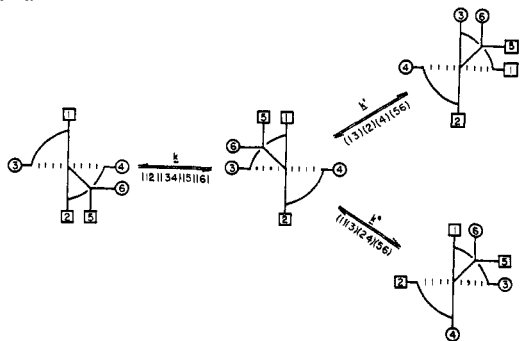
compatible. A family of possible alternative mechanisms would take place by Berry pseudorotation, utilizing one of the biphenylene carbon atoms as pivot and generating an intermediate trigonal bipyramid having the 2-isopropylphenyl moiety axial. One such mechanism is illustrated by the sequence  $6 \rightarrow 11 \rightarrow 12$ ; an-



other related possibility would use the P-4 bond as the first pivot and return to the ground state by using the P-2 bond as pivot. Without enumerating the characteristics of each of the members of this family, it is possible to point out a defect that is shared by all, they do not provide a plausible rationalization of the observed transfer of the isopropyl moiety from the face of one biphenylene moiety to that of the second. The rate of rotation around the phosphorus-2-isopropylphenyl bond in the intermediate (e.g., 11) has no influence on the rate of permutations of the type (12)(34) or (14)(23); the two biphenylene groups are not symmetry related in the intermediate, and microscopic reversibility dictates that the isopropyl group lies over the face of the same biphenylene group after the second pseudorotation as it did before the first.

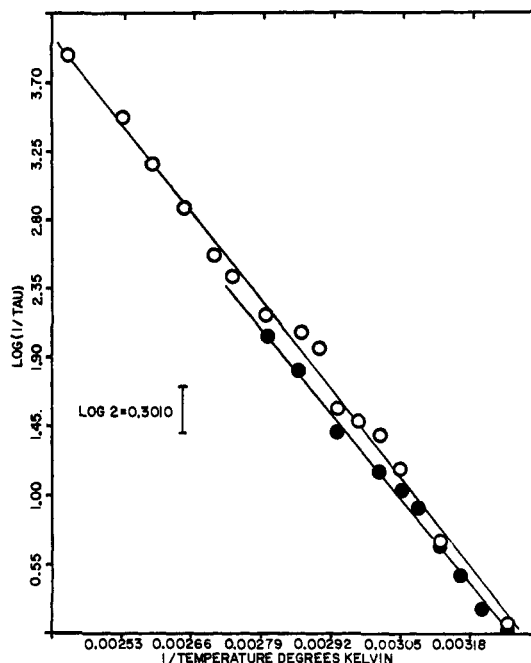
It might be possible, in principle, to remedy this defect by invoking a coincidence in rates, *viz.*, to argue that the rate of rotation around the phosphorus-2-isopropylphenyl bond in the ground state 6 is comparable to the rate of conversion of 6 to intermediates having the 2-isopropylphenyl group axial. The permutations resulting from plausible mechanisms of this type are summarized in Scheme V. In this scheme,  $k$

**Scheme V.** Pseudorotation Through an Intermediate Having a Biphenylene Moiety Bridging Two Trigonal Bipyramidal Equatorial Positions



is the rate constant for rotation of the isopropylphenyl group,  $k'$  is the rate constant for a pseudorotation generating 12 *via* 11, and  $k''$  is the rate constant for a corresponding pseudorotation using P-4 as the initial pivot. The  $K$  matrix for this scheme is given in eq 2. Since this

$$K_V = \begin{matrix} & \begin{matrix} 1 & 2 & 3 & 4 & 5 & 6 \end{matrix} \\ \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{matrix} & \begin{bmatrix} -(k + k') & k & k' & 0 & & \\ k & -(k + k'') & 0 & k'' & & \\ k' & 0 & -(k + k') & k & & \\ 0 & k'' & k & -(k + k'') & & \\ & & & & -(k' + k'') & (k' + k'') \\ & & & & (k' + k'') & -(k' + k'') \end{bmatrix} \end{matrix} \quad (2)$$



**Figure 5.** Arrhenius plot of rate data from the isopropyl resonances (open circles) and the biphenylene methyl resonances (filled circles) of 1. The activation parameters derived from a least-squares fitting to the points derived from the biphenylene methyl resonances yield  $\Delta G^\ddagger = 17.8$  kcal/mol (at 56°),  $\Delta H^\ddagger = 18.7 \pm 0.2$  kcal/mol, and  $\Delta S^\ddagger = 2.7 \pm 0.7$  eu and those from the isopropyl methyls yield  $\Delta G^\ddagger = 17.9 \pm 0.2$  kcal/mol (at 88°),  $\Delta H^\ddagger = 19.6 \pm 0.1$  kcal/mol, and  $\Delta S^\ddagger = 6.3 \pm 0.3$  eu.

matrix contains three independent variables and since, in addition, three chemical shift assignments must be tested for the biphenylene methyl groups, it is impractical to present spectra calculated for all of the variations required to find combinations that match theoretical and experimental spectra. Figure 6 contains representative spectra calculated under the simplifying assumption that  $k' = k''$ . The conclusions from these and other simulations can be briefly summarized by the qualitative statements that simulated and experimental spectra are in best agreement for  $k''/k' = 1.0$  (assuming  $k/k' = 1$ ) and for  $0.1 \lesssim k/k' \lesssim 1$  (assuming  $k'/k'' = 1$ ). Outside the ranges given, disagreement between calculated and experimental spectra are significant.

Thus, it is possible to find combinations of the rates for the processes described in Scheme V that give adequate agreement between observed and calculated spectra. However, in mechanistic terms, these combinations require an improbable coincidence of the rates of very dissimilar processes and leave unresolved the basic objections to mechanisms involving intermediates having the 2-isopropylphenyl group axial. Since we are not able to find a simple, plausible, mechanism involving such an intermediate that gives spectra that agree with the experimental spectra, we suggest

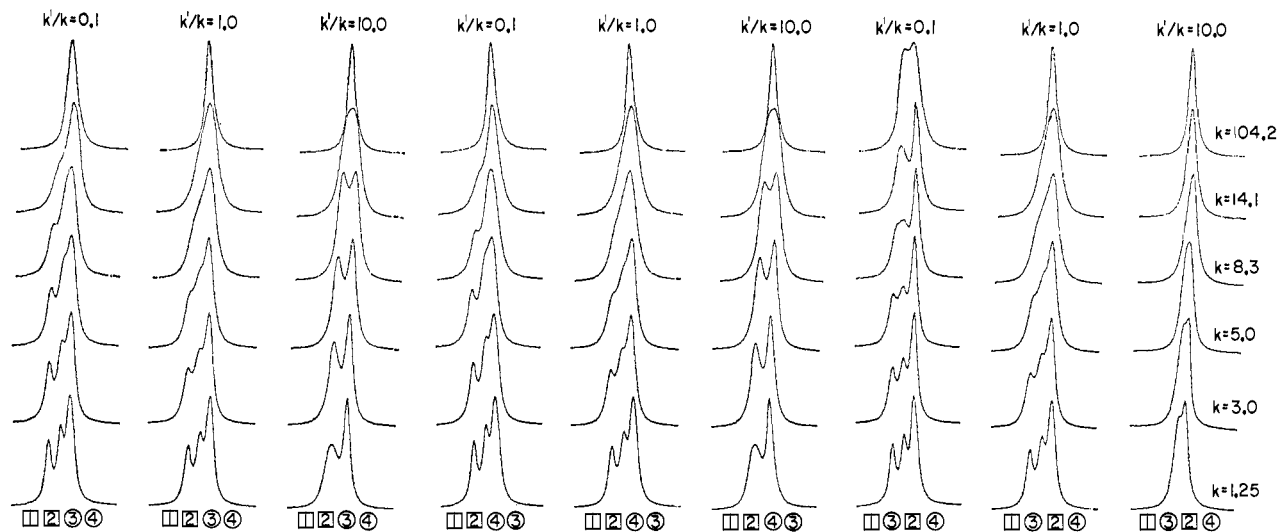


Figure 6. Spectra calculated assuming Scheme V.

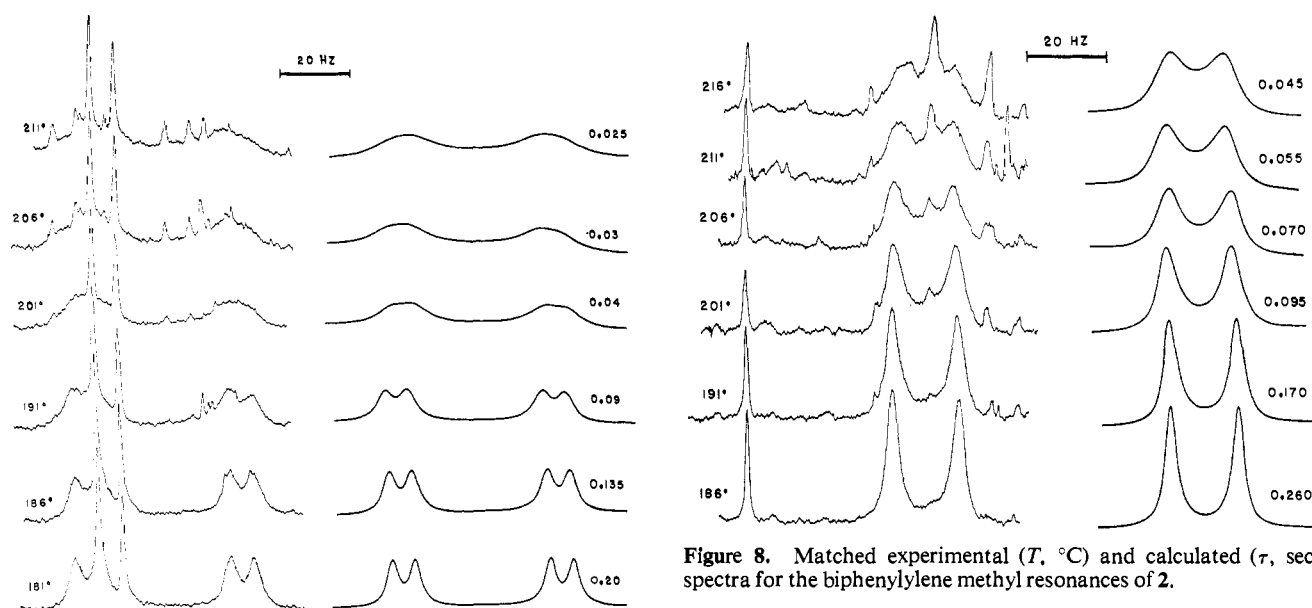


Figure 7. Matched experimental ( $T$ , °C) and calculated ( $\tau$ , sec) spectra for the isopropyl methyl resonances of **2**.

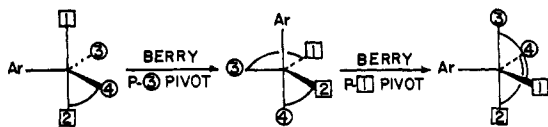
that mechanisms requiring intermediates having structures related to **11** to be discounted for the pseudorotation of **1**.

**2,4,6-Triisopropylphenylbis(4,4'-dimethyl-2,2'-biphenylene)phosphorane (2)**. Rationalization of the temperature dependence of the relatively complex spectrum of **1** required consideration of three types of processes—interchange of axial and equatorial biphenylene methyl groups, reversal of chirality at phosphorus, and rotation of the 2-isopropylphenyl group from the face of one biphenylene ring to that of a second. In an effort to check the conclusion from this work in a less complicated system, we examined the temperature dependence of the spectrum of the more symmetrical substance **2**.

The slow-exchange spectrum of **2** in the methyl region consists of two singlets, for axial and equatorial biphenylene methyls, and two doublets, for the diastereotopic isopropyl methyls. Unfortunately, pseudorotation of **2** is much slower than that of **1**, and

thermal decomposition of **2** prevented reaching the fast-exchange limiting spectra (Figures 7 and 8). Nonetheless, one interesting feature did emerge from kinetic analysis of its spectra in the intermediate exchange region; *viz.*, an Arrhenius plot of the rates of the process(es) averaging the chemical shifts of the biphenylene methyls and of the isopropyl methyls yielded approximately parallel lines separated roughly by  $\ln(2)$  (Figure 9). The reliability of this conclusion clearly rests on the quality of the spectra and is decreased by significant decomposition of **2** at temperatures greater than 200°.

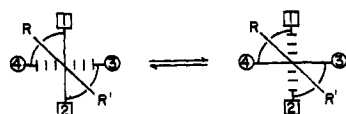
The tentative observation that the rate of reversal of chirality of **2** is twice as fast as the rate of interchange of axial and equatorial biphenylene methyl groups is inconsistent with pseudorotation characterized by the permutation of the Berry mechanism utilizing the triisopropylphenyl group as pivot; it is consistent with a mechanism generating an intermediate trigonal bipyramid with this group axial. Aside from their suggestion that the conclusions reached concerning the mechanism of pseudorotation of **1** may not extend even to the apparently very similar **2**, these rate data



must be considered sufficiently uncertain not to warrant further discussion.

### Conclusions

The central conclusion from these studies of the kinetics of pseudorotation of **1** and **2** is that for neither is the simplest version of the Berry pseudorotation mechanisms compatible with their nmr line shapes in the intermediate exchange region. For both, limiting slow-exchange spectra support the ground state structure that would have been predicted from previous work, a trigonal bipyramid, with the isopropyl substituted aryl group in an equatorial position. The simplest Berry pseudorotation that can be envisioned to occur from this starting geometry is **13**  $\rightleftharpoons$  **14**. Al-



**13**

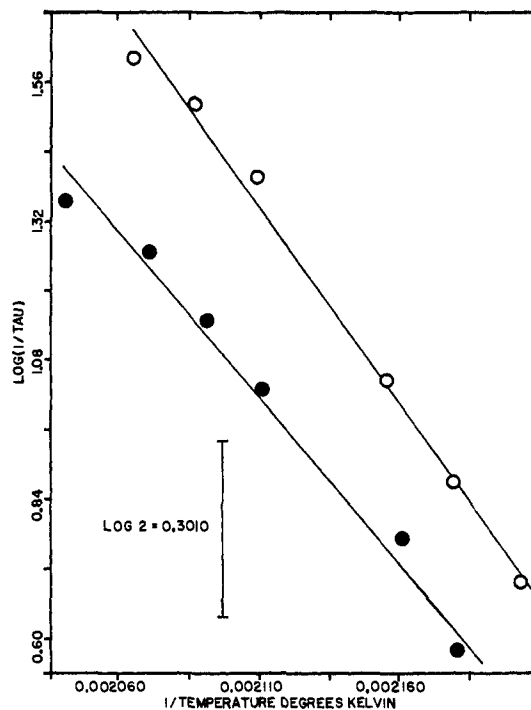
**14**

though studies of **1** argue for a permutation of sites on the biphenylene moieties that is consistent with this mechanism, the observation that the 2-isopropylphenyl moiety appears to rotate around the aryl-phosphorus bond in a process that is integrally a part of the pseudorotation suggests that a square pyramid is an intermediate along the reaction coordinate. Intermediacy of a trigonal bipyramid having an axial 2-isopropylphenyl moiety, formed by Berry pseudorotation using a biphenylene carbon-phosphorus bond as pivot, is not supported by the data for **1**. An intermediate of this type is, however, compatible with the less reliable kinetic data generated in studying **2**.

### Experimental Section

**General Methods.** All reactions involving moisture or air sensitive chemicals were carried out under inert atmospheres. Helium and prepurified nitrogen were passed through a U-tube containing calcium sulfate before use. Ether and tetrahydrofuran were distilled from lithium aluminum hydride under nitrogen immediately before use. Dioxane, hexane, and benzene were purified by distillation from a dark purple solution of disodium benzophenone dianion. Melting points were determined using a Thomas Hoover Capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. Nmr spectra were run on Varian A-60, HA-60, HA-100, or Jeolco 4H-100 spectrometers. Infrared spectra were taken in sodium chloride cells using a Perkin-Elmer Model 237B or 337 grating spectrophotometer. Mass spectra were determined on a Hitachi-Perkin-Elmer RMU-6D mass spectrometer, using a direct inlet system, by H. L. Mitchell. Microanalyses were performed by Midwest Microlabs, Indianapolis, Ind.

**Nmr Methods.** Samples were prepared by saturating the solvent system with the compound to be studied and bubbling nitrogen gas through the solution for ca. 5 min at room temperature before sealing the nmr sample tube. All the solvent systems used contained tetrachloroethane (ca. 25% by volume) as internal lock signal. Saturation of the nmr signal was checked by increasing the radiofrequency input and noting whether the peak height increased. All spectra reported in this thesis were run below saturation. For both **1** and **2** the temperature dependence of the chemical shifts was studied in the region below that in which the dynamic line broadening was important. For **2**, the biphenylene methyl chemical shift differences increased by <0.5 Hz and the



**Figure 9.** Arrhenius plots of the rate data from phosphorane **2** (open circles correspond to isopropyl methyl and filled circles to biphenylene methyl data). The activation parameters derived from a least-squares fitting to all points derived from the biphenylene methyl groups are  $\Delta G^\ddagger = 26.0 \pm 1.2$  kcal/mol (at 202°),  $\Delta H^\ddagger = 25.0 \pm 0.9$  kcal/mol, and  $\Delta S^\ddagger = -2.2 \pm 1.8$  eu and those from the isopropyl methyl are  $\Delta G^\ddagger = 25.3 \pm 1.2$  kcal/mol (at 196°),  $\Delta H^\ddagger = 30.3 \pm 0.8$  kcal/mol, and  $\Delta S^\ddagger = 10.8 \pm 1.8$  eu.

isopropyl methyl chemical shift difference by <2.0 Hz in going from 80 to 140°; for **1**, the corresponding changes over the temperature range -40 to 35° were <0.5 and <4.0 Hz.

**Bis(dimethylamine)phosphinous Chloride.** Over a 90-min period dimethylamine (100 g, 2.2 mol) was distilled into a flask equipped with a Dry Ice condenser and containing a solution of 76 g (0.552 mol) of phosphorous trichloride in 500 ml of ether. The reaction mixture was allowed to stand for 1 hr at room temperature. The liquid was removed through a sintered glass filter stick. The precipitate was washed with three 100-ml portions of ether. The combined ether layers were stirred overnight under helium in order to equilibrate the compounds formed to the bis compound. Concentration and distillation gave 63.3 g (74.5%) of product having bp 80.5-83.0° (22 mm) [lit.<sup>30</sup> bp 29° (1 mm)].

**4,4'-Dimethylbiphenyl.** 4-Methylphenylmagnesium bromide (0.58 mol, in 250 ml of THF) was added to a slurry of 133.7 g of cuprous iodide in 300 ml of tetrahydrofuran at -78° by means of a cannula. The resulting mixture was allowed to warm to room temperature over 2 hr with stirring, refluxed for 1 hr, allowed to stand overnight at room temperature, and filtered. The precipitate was washed with two 200-ml portions of ether. The solvent was removed under vacuum to give 31-33 g (60-65%) of a white, crystalline solid having mp 118-121° (lit.<sup>31</sup> 121°).

**4,4'-Dimethyl-2-nitrobiphenyl.** A mixture of 50 g of 4,4'-dimethylbiphenyl, 900 ml of nitric acid (density 1.42), and 900 ml of glacial acetic acid was stirred at 40° until the solid dissolved. The reaction mixture was then poured into 2.5 l. of water and extracted with three 400-ml portions of methylene chloride. The methylene chloride solution was washed with three 400-ml portions of water, dried (CaCl<sub>2</sub>), and concentrated under vacuum. Two recrystallizations of the residue from methanol gave 58 g (93%) of a yellowish solid, mp 63-65° (lit.<sup>32</sup> mp 59-60°).

**2-Amino-4,4'-dimethylbiphenyl.**<sup>33</sup> A mixture of 48 g (0.21 mol)

(30) H. Noeth and H. J. Vetter, *Chem. Ber.*, **96**, 1109 (1963).

(31) E. Sakellarios and Th. Kyrimis, *Chem. Ber.*, **57**, 322 (1924).

(32) E. E. J. Marler and E. E. Turner, *J. Chem. Soc.*, 2391 (1932).

(33) For more information on this reaction see "Organikum, Organisch-chemisches Grundpraktikum," Vol. 2, VEB Deutscher Verlag der Wissenschaften, Berlin, 1963, p 486.



of 4,4'-dimethyl-2-nitrobiphenyl, 400 ml of ethanol, and 26.5 ml (0.53 mol) of 100% hydrazine hydrate was heated to 35–40° and *ca.* 0.1 g of commercial Raney nickel catalyst (Grace no. 28 in water) was added. Gas was evolved immediately. When gas evolution had abated, more catalyst was added. When added catalyst did not cause gas evolution, the reaction mixture was heated to reflux for 1 hr, filtered while hot, and concentrated under vacuum. The yield was 41.5 g (*ca.* 100%) of a white solid having mp 75–77° (lit.<sup>32</sup> 62–63°):  $\nu$  (CCl<sub>4</sub>) 3465 and 3370 cm<sup>-1</sup> (–NH<sub>2</sub>). There was no nitro group absorption.

**4,4'-Dimethyl-2-iodobiphenyl.** A mixture of 40 g (0.20 mol) of 2-amino-4,4'-dimethylbiphenyl, 100 ml of concentrated hydrochloric acid, and 50 ml of water was heated to approximately 70° in order to ensure formation of the amine hydrochloride, then cooled to 0–5°. This mixture was diazotized by the slow addition of a solution of 15 g of sodium nitrite in 30 ml of water. The diazonium solution was transferred to a precooled 1.5-l. beaker in an ice bath and 32 g of potassium iodide in 50 ml of water was slowly added with stirring. The mixture was allowed to stand overnight at room temperature, then heated on a steam bath for 1 hr and cooled. The reaction mixture was extracted with one 400-ml portion of ether and the ether layer was washed with two 150-ml portions of water, one 150-ml portion of 10% sodium carbonate and one 140-ml portion of water. The ether solution was filtered, dried (CaCl<sub>2</sub>), and concentrated under vacuum. The residue was distilled to give 37.5 g (60%) of a yellowish liquid, bp 127–132° (0.17 mm) [lit.<sup>34</sup> 135–136° (0.4 mm)].

**4,4'-Dimethylbiphenylene-2,2'-iodonium Iodide.**<sup>34</sup> In a 250-ml three-necked flask equipped with magnetic stirrer, dropping funnel, condenser, and drying tube were placed 12 g of 4,4'-dimethyl-2-iodobiphenyl and 20 ml of acetic anhydride. The flask was immersed in a 30° water bath, and 12.5 ml of 40% peracetic acid was added dropwise over a 20-min period. The reaction mixture was stirred at 30° for 20 min and allowed to stand overnight at room temperature. Dropwise addition of concentrated sulfuric acid (10 ml) resulted in formation of a tan precipitate. The reaction mixture was allowed to stand at room temperature for 6 hr, poured into 350 ml of water, heated to *ca.* 45° on a steam bath, and filtered to yield a yellow solid, decomposing at about 155°. This solid was treated with 65 g of potassium iodide in 150 ml of water and heated on the steam bath for 30 min. After filtration and drying (P<sub>2</sub>O<sub>5</sub>) under vacuum for 48 hr the product (17 g, 100% crude yield) had mp 223–224° dec.

**2,2'-Diiodo-4,4'-dimethylbiphenyl.**<sup>34</sup> The 4,4'-dimethyl-2,2'-iodoniumbiphenyl iodide (13.6 g, 31.4 mmol) was heated at 230–235° for *ca.* 5 min. After cooling, the residue was triturated with three 35-ml portions of ether. The ether extracts were washed with 50 ml of 10% sodium bisulfite and 50 ml of 5% sodium carbonate, dried (CaCl<sub>2</sub>), and concentrated to give 10.25 g of crude product. The crude product was chromatographed on neutral Woelm alumina (activity I) using cyclohexane as the eluent to yield 8.1 g (59.3%) of 2,2'-diiodo-4,4'-dimethylbiphenyl having mp 110–112° after one recrystallization from ethanol–acetone.

**2-Isopropylbromobenzene.**<sup>35</sup> Triphenylphosphine (30 g, 0.115 mol) in 100 ml of anhydrous, acid-free acetonitrile was treated with enough bromine, added dropwise to the ice-bath cooled mixture, to impart a yellow tinge to the solution (*ca.* 6.1 ml, 0.10 mol). The solution was concentrated and 11 g (0.081 mol) of 2-isopropylphenol was added in one portion. The reaction mixture was heated to 270–280° for 5 hr, cooled, and subjected to steam distillation. The steam distillate was extracted with ether and the ether layer was dried (CaCl<sub>2</sub>). The ether was removed under vacuum and the residue was distilled to give 2.5 g (16.4%) of product having bp 76–82° (10 mm) [lit.<sup>36</sup> 90–93° (15 mm)].

**2-Isopropylphenylphosphinous Chloride.** 1-Bromo-2-isopropylbenzene (11.1 g, 56.0 mmol) was converted to 2-isopropylphenylbis(dimethylamino)phosphine *via* the lithium reagent and 8.65 g of chlorobis(dimethylamino)phosphine in 67.5% yield.<sup>37</sup> Reaction of the distilled (bp 77.5–79.0°, 0.1 mm) 2-isopropylphenylbis(dimethylamino)phosphine with anhydrous hydrogen chloride in ether

gave 2-isopropylphenylphosphinous chloride as a colorless liquid, bp 65–66° (0.08 mm), in 55% yield.

**2-Isopropylphenyl(4,4'-biphenylene)phosphine.** *n*-Butyllithium (27 ml of a 1.55 *N* solution in hexane) was added to a stirred solution of 9.0 g (20.8 mmol) of 2,2'-diiodo-4,4'-dimethylbiphenyl in 75 ml of ether in an ice bath at such a rate that the temperature remained at *ca.* 10°. To the resulting solution was added 4.6 g (20.8 mmol) of 2-isopropylphenylphosphinous chloride in 10 ml of ether. The resulting solution was allowed to stir at room temperature for 30 min and then worked up by concentration under vacuum and trituration of the gummy residue with water. This residue was recrystallized twice from methanol–benzene to yield a white solid having mp 114.5–116° in 35% yield: nmr (CS<sub>2</sub>, no standard)  $\delta$  6.6–8.2 (m, 10, aromatic), 1.9 (d, 6, CH(CH<sub>3</sub>)<sub>2</sub>), 2.77 (s, 6, Ar–CH<sub>2</sub>), 4.3–5.05 (m, 1, CH(CH<sub>3</sub>)<sub>2</sub>).

*Anal.* Calcd for C<sub>23</sub>H<sub>23</sub>P: C, 83.60; H, 7.02. Found: C, 82.98; H, 7.12.

**2-Isopropylphenyl(4,4'-dimethyl-2,2'-biphenylene)phosphine Tosylimine.** 2-Isopropylphenyl-4,4'-dimethylbiphenylene phosphine (2.17 g, 6.6 mmol) and 1.86 g (6.6 mmol) of anhydrous chloroamine T were mixed together in 10 ml of anhydrous dimethylformamide to give 1.85 g (61%) of a white crystalline solid having mp 238.5–241.4° after recrystallization from toluene–methanol.

*Anal.* Calcd for C<sub>30</sub>H<sub>30</sub>NO<sub>2</sub>PS: C, 72.11; H, 6.05; N, 2.80. Found: C, 71.68; H, 6.07; N, 2.77.

**2-Isopropylphenylbis(4,4'-dimethyl-2,2'-biphenylene)phosphorane (1).** The tosylimine of 2-isopropylphenyl(4,4'-dimethylbiphenylene)phosphine (0.95 g, 1.9 mmol) was added to a solution of organolithium reagent prepared from 1.5 g (3.5 mmol) of 2,2'-diiodo-4,4'-dimethylbiphenyl and 4.5 ml of 1.55 *N* *n*-butyllithium (7.0 mequiv) in 30 ml of ether. The reaction was worked up by hydrolysis and concentration, and the residue was purified by dissolving the crude product in a minimum amount of boiling tetrahydrofuran and pouring it into methanol to yield 0.70 g of a white solid having mp 231.5–232.5° (72%). The nmr spectrum of this material showed that it contained tetrahydrofuran, which could only be partially removed by pumping at 0.05 mm for 1 week. The sample used for elemental analysis was prepared by dissolving the tetrahydrofuran solvate in bromobenzene and removing tetrahydrofuran and excess bromobenzene under vacuum (0.1 mm) at room temperature to give the corresponding 2:1 bromobenzene solvate. The nmr spectrum at 33° (bromobenzene) had  $\delta$  2.60 (s, 3), 2.52 (s, 3), 2.46 (s, 6) for the biphenylene methyl protons and two doublets ( $J = 6.6$  Hz) at  $\delta$  0.98 and 1.82 for the isopropylmethyl protons: mass spectrum,  $m/e$  (rel intensity) 510 (5, M<sup>+</sup>), 509 (8), 468 (7), 467 (19, M – C<sub>3</sub>H<sub>7</sub>), 159 (7), 158 (98), 157 (8), 156 (100, bromobenzene).

*Anal.* Calcd for C<sub>50</sub>H<sub>70</sub>BrP<sub>2</sub>: C, 81.54; H, 6.42; Br, 6.78. Found: C, 81.39; H, 6.60; Br, 7.42.

**1-Bromo-2,4,6-triisopropylbenzene.** To 50 g (0.25 mol) of 1,3,5-triisopropylbenzene dissolved in 30 ml of carbon tetrachloride was added 2 g of iron powder. The reaction vessel was cooled in an ice-salt bath and light was excluded by wrapping the flask in tin foil and covering it with a towel. Bromine (41 g, 0.25 mol) in 30 ml of carbon tetrachloride was added dropwise over a 70-min period. The reaction mixture was allowed to stand overnight, washed with two 100-ml portions of water, two 50-ml portions of 20% sodium hydroxide, and one 100-ml portion of water, dried (CaCl<sub>2</sub>), and concentrated. Benzyl halide impurities in the product were destroyed by adding the crude concentrate to a solution obtained by dissolving 5 g of sodium in 100 ml of absolute ethanol. This reaction mixture was allowed to stand overnight, then diluted with 500 ml of water. The organic layer was separated, and the aqueous layer was extracted with three 100-ml portions of carbon tetrachloride. The combined organic layers were washed with two 100-ml portions of water and 100 ml of ether, dried (CaCl<sub>2</sub>), concentrated under reduced pressure, and distilled to give 52 g (73%) of product having bp 76.5–81.0° (0.08 mm) [lit.<sup>38</sup> 110–112° (4 mm)]: nmr (CCl<sub>4</sub>)  $\delta$  1.21 (d,  $J = 6.6$  Hz, 18, CH(CH<sub>3</sub>)<sub>2</sub>), 2.78 (m, 1, CH(CH<sub>3</sub>)<sub>2</sub>), 3.45 (m, 2, CH(CH<sub>3</sub>)<sub>2</sub>), and 6.84 (s, 2, aromatic).

**2,4,6-Triisopropylphenylphosphinous Dichloride.** To 20 g (0.071 mol) of 1-bromo-2,4,6-triisopropylbenzene in 75 ml of ether cooled by an ice bath was added rapidly 44 ml of 1.6 *N* *n*-butyllithium (0.071 mol). After stirring for *ca.* 1 hr at room temperature, the lithium reagent was added with stirring over 15 min to a solution of

(34) D. Hellwinkel, *Chem. Ber.*, **99**, 3660 (1966).

(35) This procedure is based on that of G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chune, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

(36) B. van Zanten and W. Th. Nauta, *Recl. Trav. Chim. Pays-Bas*, **79**, 1211 (1960).

(37) M. G. Barlow, M. Green, R. N. Haszeldine, and H. G. Higson, *J. Chem. Soc. C*, 1592 (1966); D. D. Magnelli, G. Tesi, J. U. Lowe, Jr., and W. E. McQuiston, *Inorg. Chem.*, **5**, 457 (1966).

(38) N. Rabjohn, J. S. Fronabarger, and W. W. Linstronberg, *J. Org. Chem.*, **20**, 271 (1955).

10.3 (0.075 mol) of phosphorous trichloride in 75 ml of ether that had been cooled to  $-50^{\circ}$ . The reaction was allowed to warm to room temperature and stirred for 30 min. After centrifugation, the solution was decanted and concentrated. The residue was recrystallized twice from diethyl ether at  $-45^{\circ}$  to give a granular white precipitate which was dried under vacuum for several hours at room temperature. The yield was 10.5 g (50%).

**2,4,6-Triisopropylphenyl(4,4'-dimethyl-2,2'-biphenylene)phosphine** was prepared in a manner similar to that described for its 2-isopropylphenyl analog. Dichloro-2,4,6-triisopropylphenylphosphine (5.2 g, 16.9 mmol) and 5.64 g (13 mmol) of 2,2'-diiodo-4,4'-dimethylbiphenyl gave 1.62 g (30%) of a white solid having mp  $124-126^{\circ}$ . This material crystallized only with difficulty: nmr ( $\text{CCl}_4$ , no standard)  $\delta$  2.34 (s, 6, bitolyl methyl), 1.37 (d, 18, isopropyl methyl,  $J = 7$  Hz), 6.65-7.92 (m, 8, aromatic).

*Anal.* Calcd for  $\text{C}_{29}\text{H}_{35}\text{P}$ : C, 84.02; H, 8.51. Found: C, 84.13; H, 8.23.

**2,4,6-Triisopropylphenyl(4,4'-dimethyl-2,2'-biphenylene)phosphine tosylimine** was prepared from anhydrous chloroamine T (0.02 g, 3.62 mmol) and 2,4,6-triisopropylphenyl(4,4'-dimethyl-2,2'-biphenylene)phosphine (1.5 g, 3.62 mmol) in 52% yield, mp  $227-228^{\circ}$ .

**2,4,6-Triisopropylphenylbis(4,4'-dimethyl-2,2'-biphenylene)phosphorane (2)** was prepared from the corresponding tosylimine (1.0 g, 1.72 mmol) and 2,2'-dilithio-4,4'-dimethylbiphenyl (from 1.3 g, 3 mmol, of 2,2'-diiodo-4,4'-dimethylbiphenyl and 6 mmol of 1.5 *N*-butyllithium solution). After unexceptional work-up, the crude product was purified by dissolving in a minimal amount of boiling tetrahydrofuran and pouring into methanol. The precipitate was collected as a white solid, mp  $277.5-278.5^{\circ}$ , in 30% yield.

Its nmr spectrum was recorded on a Varian HA-60 spectrometer in benzyl ether-1-chloronaphthalene using tetrachloroethane as an internal lock: mass spectrum,  $m/e$  (rel intensity) 606 (6), 605 (19, impurity), 595 (3), 594 (12, M), 593 (45), 592 (77), 552 (45), 551 (94, M - *i*-Pr), 536 (47), 535 (100, M - *i*-Pr,  $\text{C}_6\text{H}_5$ , H), 92 (20), 381 (73, M -  $\text{C}_6\text{H}_2(\textit{i-Pr})_3$ ), 212 (14), 211 (45, M - bitolyl,  $\text{C}_6\text{H}_2(\textit{i-Pr})_3$ ).

**Acknowledgments.** We wish to thank Dr. H. Lee Mitchell for running mass spectra and Dr. J. K. Krieger for extensive assistance with the computer programs. Dr. Walter Klemperer provided the information that forms the basis for Table I, as well as useful and perceptive comments on other aspects of this study. Professors Walter Thorsen and Isadore Amdur offered invaluable assistance in working out the kinetics scheme leading to  $\text{K}_{\text{III}}$ . Dr. Paul Bock kindly measured the temperature dependence of the spectrum of **1** below its slow-exchange limit.

**Supplementary Material Available.** The derivation of K matrix **1** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only on microfiche ( $105 \times 148$  mm,  $24 \times$  reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-5398.

## Metal Ion-Aromatic Complexes. XX.

### The Preparation and Molecular Structure of Anthracenetetrakis(silver perchlorate) Monohydrate

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**Abstract:** Anthracenetetrakis(silver perchlorate) monohydrate crystallizes in the monoclinic space group  $P2_1/n$  with two molecules per unit cell and with cell constants of  $a = 24.189$  (6) Å,  $b = 9.325$  (2) Å,  $c = 5.304$  (1) Å, and  $\beta = 90.35$  ( $5^{\circ}$ ). The structure was refined by full-matrix least squares including anisotropic temperature factors and anomalous dispersion corrections to a final  $R$  of 0.049. The crystal structure is made up of a three-dimensional cross-hatched network of  $\text{AgClO}_4$  and water with anthracene molecules stacked 5.3 Å apart, one above the other in the channels of the ionic network. The ionic reticulation is composed of pairs of  $\text{AgClO}_4$  chains bridged by unequal silver-water bonds to yield a two-stranded ribbon which has a ladder-like appearance. The chains are held together by weak Ag-O bonds and van der Waals forces with the ribbons separated by normal van der Waals distances. Each anthracene molecule is unequally bonded *via* its  $\pi$ -orbitals to silver atoms of four different ribbons, with the short Ag-C interactions at the 1, 4, 5, and 8 positions, rather than the expected 9, 10 positions which have the highest electron density. Each silver is four-coordinate with two interactions to two different perchlorate groups, one to a water of hydration and one to the aromatic. The trend in the Ag-C distances and associated angles indicates that the hydrated silver ion is a weaker Lewis acid than the free silver ion.

The formation of  $\text{Ag(I)}$ -aromatic complexes has now been well established both in solution studies, as reviewed by Andrews,<sup>2</sup> and by crystallographic determinations of the structures of a number of the complexes in a range of stoichiometries. One to one stoichiometries in single ring aromatics are observed in the structures of benzene (silver perchlorate)<sup>3</sup> and benzene(silver tetrachloroaluminate).<sup>4</sup> Structural studies of

complexes of the stoichiometry type  $\text{AgAr}_2^+$  which have appeared in the literature include bis(cyclohexylbenzene)(silver perchlorate),<sup>5</sup> bis(*m*-xylene)(silver perchlorate),<sup>6</sup> and bis(*o*-xylene)(silver perchlorate).<sup>7</sup> When the aromatic rings are counted independently, the

(4) R. W. Turner and E. L. Amma, *J. Amer. Chem. Soc.*, **88**, 3243 (1966).

(5) (a) E. A. Hall and E. L. Amma, *Chem. Commun.*, 622 (1968); (b) E. A. Hall Griffith and E. L. Amma, *J. Amer. Chem. Soc.*, **93**, 3167 (1971).

(6) I. F. Taylor, Jr., E. A. Hall, and E. L. Amma, *J. Amer. Chem. Soc.*, **91**, 5745 (1969).

(7) I. F. Taylor, Jr., and E. L. Amma, *Chem. Commun.*, 1442 (1970); submitted to *J. Organometal. Chem.*

(1) In partial fulfillment of the Ph.D. requirements, University of South Carolina, 1970.

(2) L. J. Andrews, *Chem. Rev.*, **54**, 713 (1954).

(3) H. G. Smith and R. E. Rundle, *J. Amer. Chem. Soc.*, **80**, 5075 (1958).