

## Transition-State Variation in the Nucleophilic Substitution Reactions of Aryl Bis(4-methoxyphenyl) Phosphates with Pyridines in Acetonitrile

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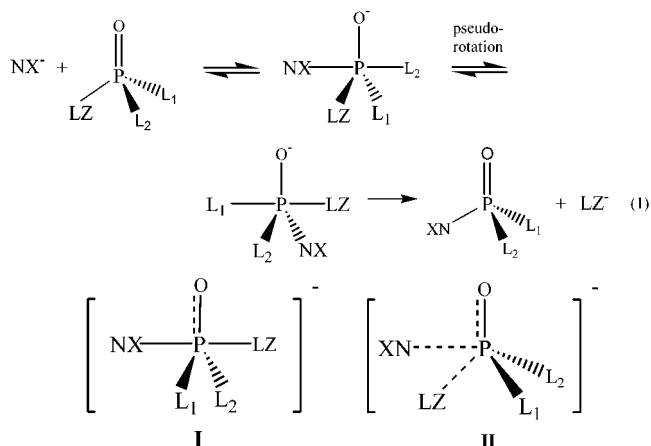
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The kinetics and mechanism of the reactions of Z-aryl bis(4-methoxyphenyl) phosphates, (4-MeOC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>P(=O)OC<sub>6</sub>H<sub>4</sub>Z, with pyridines (XC<sub>5</sub>H<sub>4</sub>N) are investigated in acetonitrile at 55.0 °C. In the case of more basic phenolate leaving groups (Z = 4-Cl, 3-CN), the magnitudes of  $\beta_X$  ( $\beta_{\text{nuc}}$ ) and  $\beta_Z$  ( $\beta_{\text{lg}}$ ) indicate that mechanism changes from a concerted process ( $\beta_X = 0.22$ – $0.36$ ,  $\beta_Z = -0.42$  to  $-0.56$ ) for the weakly basic pyridines (X = 3-Cl, 4-CN) to a stepwise process with rate-limiting formation of a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate ( $\beta_X = 0.09$ – $0.14$ ,  $\beta_Z = -0.08$  to  $-0.28$ ) for the more basic pyridines (X = 4-NH<sub>2</sub>, 3-CH<sub>3</sub>). This proposal is supported by a large negative cross-interaction constant ( $\rho_{XZ} = -1.98$ ) for the former and a positive  $\rho_{XZ}$  (+0.97) for the latter processes. In the case of less basic phenolate leaving groups (Z = 3-CN, 4-NO<sub>2</sub>), the unusually small magnitude of  $\beta_Z$  values is indicative of a direct backside attack TBP-5C TS in which the two apical sites are occupied by the nucleophile and leaving group, ap(NX)–ap(LZ). The instability of the putative TBP-5C intermediate leading to a concerted displacement is considered to result from relatively strong proximate charge transfer interactions between the  $\pi$ -lone pairs on the directly bonded equatorial oxygen atoms and the apical bond ( $n_{\text{O}}(\text{eq}) - \sigma^*(\text{ap})$ ). These are supported by the results of natural bond orbital (NBO) analyses at the NBO-HF/6-311+G\*\*//B3LYP/6-311+G\*\* level of theory.

### Introduction

The great interest in phosphorus chemistry stems from its relevance to biological chemistry and from its usefulness in synthesis. Two main types of displacement process are known in neutral phosphoryl group transfer reaction.<sup>1</sup> The stepwise mechanism involves a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate and the concerted displacement at phosphorus through a single pentacoordinate transition state (TS).<sup>1,2</sup> In the former, the addition step can precede the elimination (addition–elimination) or it can be reversed to elimination–addition.<sup>1</sup> There is a further complication involving stereochemical results since inversion or retention of configuration can be obtained depending on whether the attacking nucleophile (NX) and leaving group (LZ) occupy the apical positions (I: ap(NX)–ap(LZ)) or an apical and an equatorial positions (ap(NX)–eq(LZ)) in the TBP-5C adduct. In the latter case, a Berry type pseudorotation (BPR)<sup>3</sup> leads subsequently to an eq(NX)–ap(LZ) adduct, eq 1. In the concerted retention process, a front-side nucleophilic attack occurs, II.



The change in mechanism from a concerted to a stepwise reaction has been shown to occur by varying the strength of the nucleophile and leaving group in the neutral phosphoryl group transfer.<sup>4</sup> The concerted path becomes more likely to be followed with less basic (or weaker) nucleophiles and with stronger apicophilic (or nucleofugal) leaving group. For very basic (or strong) nucleophiles and poor (less nucleofugal) leaving groups (e.g., PhO<sup>−</sup>), a stepwise path is favored with an ap(NX)–eq(LZ) type TBP-5C adduct that pseudorotates before loss of the leaving group to an eq(NX)–ap(LZ) form.<sup>4</sup>

In this work, we examined mechanistic changes involved in the nucleophilic substitution of aryl bis(4-

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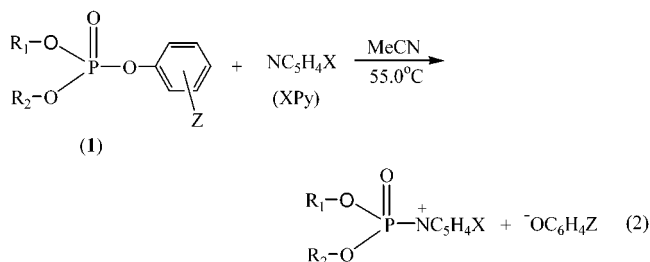
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**Table 1. Second-Order Rate Constants ( $k_2 \times 10^4/\text{M}^{-1} \text{s}^{-1}$ ) for the Reactions of Z-Aryl Bis(4-methoxyphenyl) Phosphates with X-Pyridines in Acetonitrile at 55.0 °C**

X	Z				
	4-Cl	3-Cl	3-CN	4-CN	4-NO <sub>2</sub>
4-NH <sub>2</sub>	67.0	75.1	85.1	88.3	91.2
4-CH <sub>3</sub>	24.0	34.7	46.8	46.6	49.2
4-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	21.4	29.0	40.7	43.7	45.7
3-CH <sub>3</sub>	20.0	27.2	38.0	42.8	44.7
H	7.17	7.58	8.12	8.55	9.03
3-Cl	0.418	0.790	2.31	2.63	2.88
3-CH <sub>3</sub> CO	0.392	0.776	2.03	2.14	2.57
4-CH <sub>3</sub> CO	0.273	0.423	1.21	1.26	1.41
3-CN	0.248	0.361	1.03	1.07	1.12
4-CN	0.198	0.268	0.679	0.708	0.776

methoxyphenyl) phosphates (1), with pyridines in acetonitrile at 55.0 °C, eq 2, by determining the Hammett



$R_1 = R_2 = 4\text{-MeOC}_6\text{H}_4$ .

Z = 4-Cl, 3-Cl, 3-CN, 4-CN, 4-NO<sub>2</sub>.

X = 4-NH<sub>2</sub>, 4-CH<sub>3</sub>, 4-C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, 3-CH<sub>3</sub>, H, 3-Cl, 3-CH<sub>3</sub>CO, 4-CH<sub>3</sub>CO, 3-CN, 4-CN.

( $\rho_X$ ,  $\rho_Z$ ) and Brönsted ( $\beta_X$ ,  $\beta_Z$ ) type selectivity parameters including the cross-interaction constants,<sup>5</sup>  $\rho_{XZ}$ , eqs 3, where X and Z represent substituents in the nucleophile (NX) and leaving group (LZ), respectively. To substantiate our arguments theoretically, we have carried out density functional theory (DFT) calculations on various TBP-5C adduct structures.

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \quad (3a)$$

$$\rho_{XZ} = \frac{\partial\rho_Z}{\partial\sigma_X} = \frac{\partial\rho_X}{\partial\sigma_Z} \quad (3b)$$

## Results and Discussion

The reactions were carried out under pseudo-first-order conditions with a large excess of pyridine. The pseudo-first-order rate constants observed ( $k_{\text{obs}}$ ) for all the reactions followed eq 4

$$k_{\text{obs}} = k_0 + k_2[\text{Py}] \quad (4)$$

with negligible  $k_0$  ( $= 0$ ) in acetonitrile. The second-order rate constants,  $k_2$  ( $\text{M}^{-1} \text{s}^{-1}$ ), summarized in Table 1 were determined using eq 4 with at least five pyridine concentrations, [Py]. No third-order or higher-order terms were detected, and no complications arising from side reaction were found in the determination of  $k_{\text{obs}}$  and in the linear plots of eq 4. This suggests that the overall reaction follows cleanly the route given by eq 2.

The rate constants  $k_2$  are correlated by the Brönsted plots in Figures 1 and 2. The Brönsted coefficients ( $\beta_X$ ,

**Table 2. Selectivity Parameters<sup>a</sup>  $\rho_X$ ,  $\beta_X$ ,  $\rho_Z$ ,  $\beta_Z$ , and  $\rho_{XZ}$  for the Reactions of Z-Aryl Bis(4-methoxyphenyl) Phosphates with X-Pyridines in Acetonitrile at 55.0 °C**

X	(Z = 4-Cl, 3-CN)		(Z = 3-CN, 4-NO <sub>2</sub> )	
	$\rho_Z$	$\beta_Z$	$\rho_Z$	$\beta_Z$
4-NH <sub>2</sub>	0.30 ± 0.02 <sup>b</sup>	-0.08 ± 0.01	0.13 ± 0.03	-0.01 ± 0.001
4-CH <sub>3</sub>	0.87 ± 0.13	-0.21 ± 0.06	0.09 ± 0.05	-0.01 ± 0.005
4-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	0.85 ± 0.04	-0.28 ± 0.02	0.22 ± 0.03	-0.02 ± 0.001
3-CH <sub>3</sub>	0.84 ± 0.06	-0.21 ± 0.04	0.30 ± 0.08	-0.02 ± 0.004
	$\rho_{XZ} = 0.97 \pm 0.15$		$\rho_{XZ} = 0.18 \pm 0.14$	
3-Cl	2.25 ± 0.12	-0.56 ± 0.04	0.43 ± 0.06	-0.03 ± 0.01
3-CH <sub>3</sub> CO	2.18 ± 0.02	-0.53 ± 0.07	0.44 ± 0.13	-0.03 ± 0.01
4-CH <sub>3</sub> CO	1.96 ± 0.28	-0.50 ± 0.01	0.31 ± 0.07	-0.02 ± 0.01
3-CN	1.91 ± 0.32	-0.47 ± 0.02	0.17 ± 0.01	-0.01 ± 0.001
4-CN	1.63 ± 0.33	-0.42 ± 0.03	0.26 ± 0.04	-0.02 ± 0.01
	$\rho_{XZ} = -1.98 \pm 0.77$		$\rho_{XZ} = -0.81 \pm 0.7$	

Z	(X = 4-NH <sub>2</sub> ~ 3-CH <sub>3</sub> )	
	$\rho_X$	$\beta_X$
4-Cl	-0.89 ± 0.02	0.14 ± 0.003
3-Cl	-0.74 ± 0.04	0.12 ± 0.008
3-CN	-0.57 ± 0.03	0.09 ± 0.006
4-CN	-0.54 ± 0.01	0.09 ± 0.02
4-NO <sub>2</sub>	-0.53 ± 0.02	0.09 ± 0.02

Z	(X = 3-Cl ~ 4-CN)	
	$\rho_X$	$\beta_X$
4-Cl	-1.11 ± 0.07	0.22 ± 0.02
3-Cl	-1.67 ± 0.13	0.35 ± 0.01
3-CN	-1.77 ± 0.09	0.36 ± 0.05
4-CN	-1.86 ± 0.15	0.36 ± 0.05
4-NO <sub>2</sub>	-1.96 ± 0.11	0.39 ± 0.05

<sup>a</sup>  $\sigma$  values were taken from: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. The  $pK_a$  values of pyridines in water at 25 °C were taken from ref 7 and: Dean, J. A. *Handbook of Organic Chemistry*; McGraw-Hill: New York, 1987; Chapter 8. The  $pK_a$  values of phenols in CH<sub>3</sub>CN at 25 °C were taken from ref 8, and the  $pK_a$  value of 3-cyanophenol was determined by eq 5b. <sup>b</sup> Standard deviations.

$\beta_Z$ ) derived from the linear portion of these plots and Hammett coefficients ( $\rho_X$ ,  $\rho_Z$ ) are summarized in Table 2. It is noted that all the plots, Figures 1 and 2, are biphasic with break points at X = H and Z = 3-CN, respectively, in the variation of the nucleophile and leaving group. For the more basic (stronger) nucleophiles (X = 4-NH<sub>2</sub>, 3-CH<sub>3</sub>), the magnitudes of  $\rho_X$  ( $= -0.53$  to  $-0.89$ ) and  $\beta_X$  ( $= 0.09$ – $0.14$ ) are smaller than those for the less basic (weaker) nucleophiles (X = 3-Cl, 4-CN) ( $\rho_X = -1.11$  to  $-1.96$  and  $\beta_X = 0.22$ – $0.39$ ). Similarly, for the former (stronger nucleophiles), the magnitudes of  $\rho_Z$  and  $\beta_Z$  are smaller than those for the latter less basic (weaker) nucleophiles. On the other hand, the magnitudes of  $\rho_Z$  and  $\beta_Z$  are also in two distinct groups with larger values for more basic (poorer) leaving groups (Z = 4-Cl, 3-CN) and smaller ones for less basic (better) leaving groups (Z = 3-CN, 4-NO<sub>2</sub>).

It should be noted that in the determination of the Brönsted coefficients,  $\beta_X$ , we correlated  $\log k_2$  (MeCN) with  $pK_a(\text{H}_2\text{O})$  of pyridines, which has been shown to be justified.<sup>6</sup> For the determination of  $\beta_Z$  values, however, we have tried correlations of  $\log k_2(\text{MeCN})$  with both the

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$pK_a(\text{H}_2\text{O})^7$  and  $pK_a(\text{MeCN})^8$  values of phenols. Available  $pK_a$  values gave the following relations, eqs 5, for phenols. These relations indicate that the Brønsted basicities of phenolates change by ca. twice in acetonitrile relative to those in water ( $\delta pK_a(\text{MeCN})/\delta pK_a(\text{H}_2\text{O}) \cong 2.1$ ) for a given substituent changes ( $\delta\sigma$ ). In contrast, however, the ratio of  $\beta_Z$ , i.e., changes in rates ( $\delta \log k_2$ ) (Lewis basicities) with  $pK_a$ 's for a given substituent changes ( $\delta pK_a$ ) are only an average of 1.6 ( $= \beta_Z$  with  $pK_a(\text{H}_2\text{O})/\beta_Z$  with  $pK_a(\text{MeCN})$ ); i.e., the ratios differ by a factor of ca. 0.76 ( $= 1.6/2.1$ ). This is of course due to the partial bond cleavage (or formation) of phenolate anions in the rate-determining step (in the TS) in contrast to the complete deprotonation (or protonation) in the  $pK_a$  measurements of pyridines.

$$pK_a(\text{H}_2\text{O}) = (-2.11 \pm 0.08)\sigma^- + 9.89 \pm 0.05; \\ r = 0.960, N = 8 \quad (5a)$$

$$pK_a(\text{MeCN}) = (-4.35 \pm 0.09)\sigma^- + 26.58 \pm 0.09; \\ r = 0.998, N = 12 \quad (5b)$$

Regarding the biphasic linear free energy relationships with nucleophile variation,  $\rho_X$  ( $\rho_{\text{nuc}}$ ) and  $\beta_X$  ( $\beta_{\text{nuc}}$ ), we propose mechanistic change from a concerted (with less basic pyridines) to a stepwise mechanism with rate-limiting formation of a TBP-5C intermediate,  $\text{T}^\pm$  (with more basic pyridines), based on the following grounds: (i) It is generally known that the concerted path is favored by weakly basic nucleophiles while the stepwise path is favored by strongly basic nucleophiles.<sup>4,9</sup> (ii) The sign of  $\rho_{XZ}$  is negative ( $\rho_{XZ} = -1.98$  for weakly basic nucleophiles) for the concerted paths but is positive for the stepwise processes ( $\rho_{XZ} = 0.97$  for strongly basic nucleophiles) in accordance with the mechanistic criteria established based on theoretical<sup>10</sup> as well as experimental results.<sup>5,11</sup> (iii) The magnitudes of  $\beta_X$  and  $\beta_Z$  values are relatively large for weakly basic nucleophiles ( $\beta_X = 0.22-0.39$ ,  $\beta_Z = -0.42$  to  $-0.56$ ). Although the  $\beta_X$  values in the range 0.4–0.7 are obtained for most of the concerted displacement reactions at the carbonyl carbon<sup>12</sup> and phosphoryl P centers,<sup>13</sup> some  $\beta_X$  values smaller than 0.4

for concerted processes have been reported in phosphoryl group transfer reactions.<sup>14</sup> Skoog and Jencks<sup>14a</sup> reported  $\beta_X = 0.17$  and 0.19 for the concerted reactions of pyridines with phosphorylated 3-methoxypyridine and  $\beta_X = 0.22$  and 0.28 for the reaction with phosphorylated 4-morpholinopyridine, respectively. Williams and co-workers<sup>14b</sup> obtained  $\beta_X = 0.15$  for the similar concerted reaction. Williams and co-workers<sup>14d</sup> reported also the similar magnitudes of  $\beta_X$  ( $= 0.14-0.60$ ) and  $\beta_Z$  ( $= -0.52$  to  $-0.81$ ) values for the concerted reactions of phenolate anions with phenyl diphenyl phosphate ( $(\text{PhO})_2\text{P}(\text{=O})\text{OAr} + \text{ArO}^-$ ). These are certainly similar to or even smaller than the  $\beta_X$  values obtained for the weakly basic nucleophiles in the present work. It should be noted, however, that  $\beta_X$  values larger than 0.7 have been also found in other concerted reactions.<sup>15</sup> On the other hand, the magnitudes of  $\beta_X$  and  $\beta_Z$  values in a stepwise mechanism with the rate-limiting bond formation of  $\text{T}^\pm$  are in general substantially smaller ( $\beta_X = 0.0-0.3$  and  $\beta_Z = -0.1$  to  $-0.3$ )<sup>16</sup> than those for the concerted reactions. For example,  $\beta_X$  values in the range  $\beta_X = 0.19-0.23$  have been obtained for the stepwise reactions with rate-limiting bond making in the pyridinolysis of *S*-phenyl 4-nitrobenzoates in acetonitrile,  $\text{XC}_5\text{H}_4\text{N} + 4\text{-NO}_2\text{C}_6\text{H}_4\text{C}(\text{=O})\text{SC}_6\text{H}_4\text{Z}$ .<sup>11e</sup> Senatore et al.<sup>2b,17</sup> obtained a biphasic rate dependence on the basicity of nucleophiles in the reaction of alkoxides and phenoxides with aryl methanesulfonates ( $\text{CH}_3\text{S}(\text{=O})\text{OAr}$ ), which indicated a mechanistic changeover from a breakdown ( $\beta_X = 0.79$ ) to formation ( $\beta_X \cong 0.0$ ) of TBP intermediate as the basicity of the nucleophile is increased. The  $\beta_X$  of near zero is even smaller than the values obtained ( $\beta_X = 0.09-0.14$ ) with the strongly basic nucleophiles in Table 2. Since in the rate-limiting formation of  $\text{T}^\pm$  the central atom (P)–leaving group (OAr) bond should not break but relax somewhat, the  $\beta_Z$  values should be much smaller than those in the concerted processes where the leaving group bond is mostly broken and the nucleophile-phosphorus bond is mostly formed in the TS. (iv) The unusually large negative  $\rho_{XZ}$  value for the weakly basic nucleophiles ( $\rho_{XZ} = -1.98$ ) is indicative of a TS formed by the concerted front-side nucleophilic attack,<sup>18</sup> **II**, since the nucleophile and leaving group can be in close proximity in such TS. Although we have no conclusive proof for this proposal, there are evidence<sup>18b</sup> in support of such structural dependence of the large negative  $\rho_{XZ}$  as we have advanced in connection with the frontside attack  $\text{S}_\text{N}2$  TS structures for the anilinolysis of 1- ( $\rho_{XZ} = -0.56$ )<sup>19a</sup> and 2-phenylethyl ( $\rho_{XZ} = -0.45$ )<sup>19b</sup> and

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**Table 3. Comparison of Bond Length (Å) in Phosphates with Y (F or Cl) and R (CH<sub>3</sub> or OCH<sub>3</sub>) as Ligands Calculated at the B3LYP/6-311+G\*\* Level**

YPO(R) <sub>2</sub>		+ Y <sup>-</sup> → [Y <sub>2</sub> PO(R) <sub>2</sub> ] <sup>-</sup>		
Reactant		TBP-5C adduct (A)		
		TBP-5C adduct		
reactant		(2A) [F <sub>2</sub> PO(CH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>		Δd(ax - eq)
(2) FPO(CH <sub>3</sub> ) <sub>2</sub>		ax	eq	
<i>d</i> <sub>P-O<sup>a</sup></sub>	1.811	1.895	1.845	+0.050
<i>d</i> <sub>P-F</sub>	1.619	1.828	1.752	+0.076
		(3A) [F <sub>2</sub> PO(OCH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>		
(3) FPO(OCH <sub>3</sub> ) <sub>2</sub>		ax	eq	Δd(ax - eq)
<i>d</i> <sub>P-O<sup>a</sup></sub>	1.585	1.695	1.663	+0.032
<i>d</i> <sub>P-F</sub>	1.599	1.736	1.714	+0.022
		(4A) [Cl <sub>2</sub> PO(OCH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>		
(4) ClPO(OCH <sub>3</sub> ) <sub>2</sub>		ax	eq	Δd(ax - eq)
<i>d</i> <sub>P-O<sup>a</sup></sub>	1.590	1.660	1.599	+0.061
<i>d</i> <sub>P-Cl</sub>	2.074	2.487	2.398	+0.089

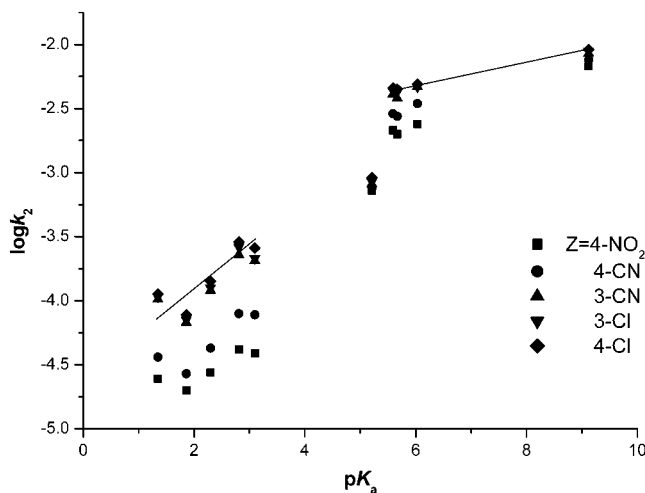
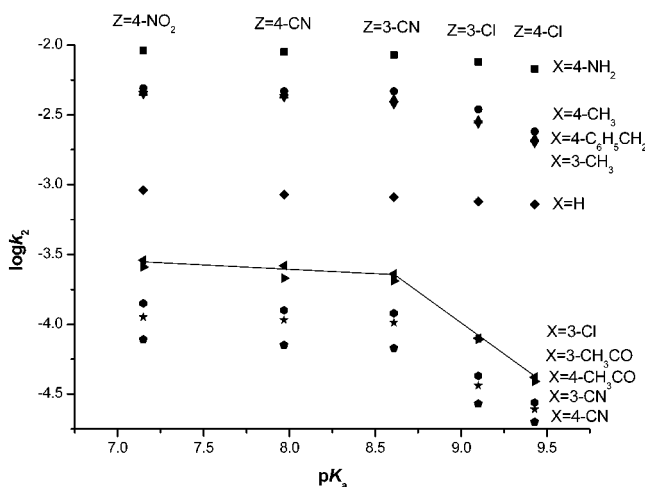
<sup>a</sup> Distance between P and R.

cumyl arenesulfonates ( $\rho_{XZ} = -0.75$ ).<sup>19c</sup> Frontside attack by the nucleophile should lead to retention of configuration as shown in **II**. (v) The relatively smaller magnitudes of  $\rho_Z$  and  $\rho_{XZ}$  values for the stronger nucleofuge (or less basic phenoxides) with Z = 3-CN, 4-NO<sub>2</sub> suggest backside nucleophilic attack since the more apicophilic (or the stronger) the leaving group, the lower the energy is for the concerted path, i.e., the more likely is the backside attack with an ap(NX)-ap(LZ) TS structure, **I**, accompanied by an inversion of configuration.<sup>4</sup> In this structure, both the nucleophile and leaving group are on the apical sites so that both the XN-P and P-LZ bonds are longer than those for an equatorial site. The longer distance involved in the TS leads to smaller magnitudes of both  $\rho_Z$ ,  $\beta_Z$  and  $\rho_{XZ}$ .<sup>5,20</sup> It is known that pentacoordinate species have apical bonds that are significantly longer than regular single bonds.<sup>4,13a,21</sup>

In Table 3, bond length changes are compared for three selected model systems, FPO(CH<sub>3</sub>)<sub>2</sub>, (**2**), FPO(OCH<sub>3</sub>)<sub>2</sub>, (**3**), and ClPO(OCH<sub>3</sub>)<sub>2</sub>, (**4**), calculated at the B3LYP/6-311+G\*\* level.<sup>22</sup> These three systems represent those without lone pair for *n* -  $\sigma^*$  charge transfer change (**2**), and with lone pair (*n*) for the *n* -  $\sigma^*$  charge-transfer interaction between *n* and  $\sigma^*$  orbitals of axial bonds (**3** and **4**); in the former (**3**), the  $\sigma_{P-F}^*$  level is very much higher ( $\sigma_{P-F}^* = 0.6589$  au) than the  $\sigma_{P-Cl}^*$  level ( $\sigma_{P-Cl}^* = 0.2268$  au) in the latter (**4**), Table 4. In all cases, all of the bonds including the P=O bond stretch in the TBP-5C adduct where P=O becomes a single bond (P-O<sup>-</sup>). For example, the P-F bond in (**2**) extends by more than 0.2 Å on going from the reactant to the axial P-F bond in the TBP-5C adduct. Again we note that the axial bonds

**Table 4. MO Levels ( $\epsilon$  in Au) for **3** and **4** Calculated at the NBO-HF/6-311+G\*\*//B3LYP/6-311+G\*\* Level**

Y	MO	$\epsilon$ (au)
F	<i>n</i> <sub>O</sub> (sp <sup>2</sup> )	-0.8215
	<i>n</i> <sub>O</sub> (p)	-0.5446
	$\sigma$ (P-F)	-1.1712
	$\sigma^*$ (P-F)	+0.6589
Cl	<i>n</i> <sub>O</sub> (sp <sup>2</sup> )	-0.8188
	<i>n</i> <sub>O</sub> (p)	-0.5471
	$\sigma$ (P-Cl)	-0.8056
	$\sigma^*$ (P-Cl)	+0.2268

**Figure 1.** Plot of  $\log k_2$  vs  $pK_a$  (X-pyridines, in H<sub>2</sub>O) for the reactions of Z-aryl bis(4-methoxyphenyl) phosphates with X-pyridines in acetonitrile at 55.0 °C.**Figure 2.** Plot of  $\log k_2$  vs  $pK_a$  (Z-phenols, in H<sub>2</sub>O) for the reactions of Z-aryl bis(4-methoxyphenyl) phosphates with X-pyridines in acetonitrile at 55.0 °C.

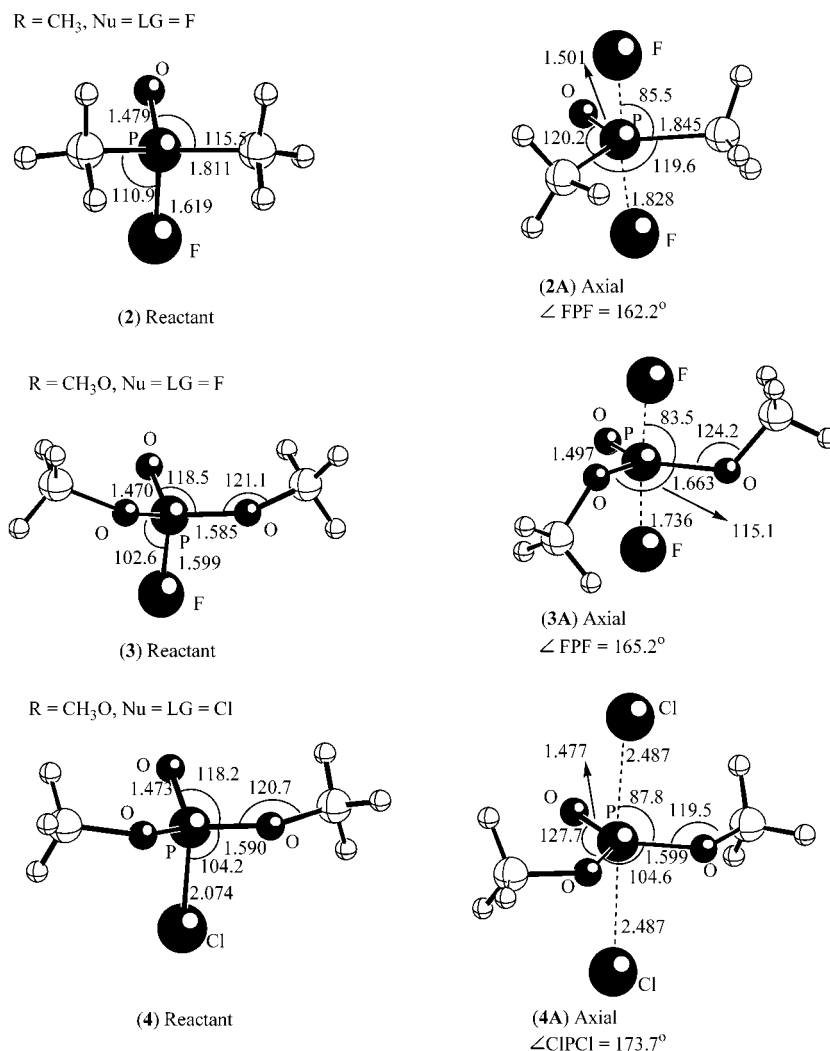
are longer than the corresponding equatorial bonds, especially for *d*<sub>P-Cl</sub> the difference is the greatest with  $\Delta d(ax-eq) = 0.089$  Å. In other words, the lower the  $\sigma^*$  level, the longer is the axial than the equatorial bond (vide infra).

Our density functional theory (DFT) results at the B3LYP/6-311+G\*\* level<sup>22</sup> show that the TBP-5C adducts, (**2A**) ~ (**4A**) in Figure 3, have axial P-Y (where Y = F or Cl) conformations. Interestingly, however, the p lone pair (*n*<sub>O</sub>(p)) on the equatorial methoxy oxygen atom in (**3A**) adopts a preferred orientation that is perpendicular (L) to the apical axis, **III**, in contrast that in (**4A**) adopts the

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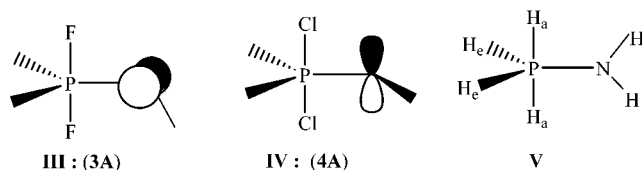
(21) (a) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, 96, 6735. (b) Ramirez, F. *Acc. Chem. Res.* **1968**, 1, 168. (c) McDowell, R. S.; Streitwieser, A. *J. Am. Chem. Soc.* **1985**, 107, 5849. (d) Lee, I.; Kim, C. K.; Lee, B.-S.; Ha, T.-K. *THEOCHEM* **1993**, 279, 191.

(22) (a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785. (c) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian Inc.: Pittsburgh, 1993.



**Figure 3.** Structures of reactants **2–4** and TBP-5C adducts (**2A–4A** calculated at the B3LYP/6-311+G\*\* level (bond lengths in Å, and angles in deg).

conformation in which the p orbital axis is parallel (||) with the apical axis, **IV**.



The bonding in PH<sub>4</sub>NH<sub>2</sub>, where N has a p lone pair  $n_N(p)$ , has been discussed by many authors.<sup>21,23</sup> In this compound, **V**, the second-order perturbation energy,  $\Delta E_{\sigma-\sigma^*}^{(2)}$  in eq 6<sup>24</sup> where  $\sigma$  and  $\sigma^*$  represent bonding ( $n$ ,  $\pi$ , or  $\sigma$ ) and antibonding ( $\pi^*$  or  $\sigma^*$ ) orbitals, respectively, in general and  $F$  is the Fock operator, has been shown to be much more stabilizing in perpendicular ( $\perp$ )  $n_N(p)$  form rather than in parallel (||)  $n_N(p)$  form.<sup>21a,23,25</sup>

(23) (a) Strich, A.; Veillard, A. *J. Am. Chem. Soc.* **1973**, *95*, 5574. (b) Wang, P.; Zhang, Y.; Glaser, R.; Reed, A. E.; Schleyer, P. v. R.; Streitwieser, A. *J. Am. Chem. Soc.* **1991**, *113*, 55.

(24) (a) Epitotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Structural Theory of Organic Chemistry*; Springer-Verlag: Berlin, 1977; Part I. (b) Reed, R. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (c) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1988**, *19*, 610. (d) Glendening, E. D.; Badenhop, J. K.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628.

$$\Delta E_{\sigma-\sigma^*}^{(2)} = - \frac{2 \langle \sigma | F | \sigma^* \rangle^2}{\epsilon_{\sigma^*} - \epsilon_{\sigma}} \quad (6)$$

This was ascribed to the following: (i) larger  $n(\perp) - \sigma_{P-\text{He}}^*$  charge-transfer energies (eq 6) than the  $n(\parallel) - \sigma_{P-\text{Ha}}^*$  interaction energies<sup>23c</sup> due to the higher  $\sigma_{P-\text{Ha}}^*$  (wider  $\Delta\epsilon = \epsilon_{\sigma^*} - \epsilon_n$  in eq 6) rather than  $\sigma_{P-\text{He}}^*$  level even though overlap between  $n(\parallel)$  and P-H<sub>a</sub> is known to be greater (and hence the matrix element,  $F_{n\sigma^*}$ , is greater in eq 6) than that between  $n(\perp)$  and P-H<sub>e</sub>; and (ii) larger exclusion repulsion energies<sup>21a,23b,25</sup> included in the no-charge-transfer term ( $\Delta E_{\text{NCT}}$ ) in eq 7<sup>24b</sup> where  $\Delta E_{\text{CT}}$  is the total  $\sigma-\sigma^*$  charge-transfer energies  $\Delta E_{\sigma-\sigma^*}^{(2)}$  in eq 6. The  $\Delta E_{\text{NCT}}$  term includes also energies due to electrostatic (induction and polarization) interactions<sup>24b</sup> and is the Lewis energy,  $E_{\text{Lew}}$ , associated with the localized Hartree-Fock wave function<sup>26</sup> (corresponding essentially to a Lewis structure). The  $\sigma_{\text{AB}} - \sigma_{\text{CD}}^*$  NBO delocalization leads to a decrease in A-B and C-D bond orders (and hence weaken A-B and C-D bonds) and a simultaneous increase in B-C bond order<sup>24</sup> (strengthen B-C bond).

(25) Hoffmann, R.; Howell, J. M.; Muettterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3057.

(26) Carballeira, L.; Perez-Juste, I. *J. Phys. Chem. A* **2000**, *104*, 9362.

$$\Delta E = E(\text{TBP-5C}) - E(\text{separated reactants}) = \Delta E_{\text{CT}} + \Delta E_{\text{NCT}} \quad (7)$$

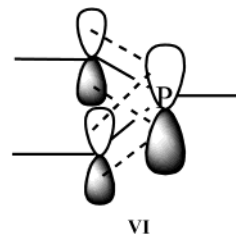
The bond–bond ( $\sigma$ – $\sigma$ ) four-electron (exclusion) repulsion interaction is greater in the  $n(\parallel)$ – $\sigma_{\text{P-Ha}}$  interaction since overlap between the two interacting orbitals is greater than that in the  $n(\perp)$ – $\sigma_{\text{P-He}}$  interaction. The  $\sigma$ – $\sigma$  four-electron repulsion is strongly dependent on the overlap between the two interacting orbitals.<sup>24a</sup> These two factors are also responsible for the preferred  $n(\perp)$  and  $n(\parallel)$  conformations of the oxygen p lone pair in **3A** and **4A**, respectively (Figure 3). For **3A**, the level gap is  $\Delta\epsilon = \epsilon_{\sigma^*} - \epsilon_n = 1.2035$  au, whereas that for **4A** is  $\Delta\epsilon = 0.7739$ , and hence, the  $n$ – $\sigma^*$  charge-transfer stabilization energies in **3A** should be much smaller than that in **4A** due to the much larger energy gap in eq 6. On the other hand, however, since the overlap in the  $n(\parallel)$  forms is much greater and hence the exclusion repulsion destabilization should be much greater in this form. Due to the large destabilization of  $n(\parallel)$ – $\sigma_{\text{P-F}}$  and smaller  $n(\parallel)$ – $\sigma_{\text{P-F}}^*$  charge-transfer stabilization, that are expected from the results on  $\text{PH}_4\text{NH}_2$  (vide supra), **3** will be forced to take  $n(\perp)$  structure of **3A**. In contrast for **4**, the  $n(\parallel)$ – $\sigma_{\text{P-Cl}}^*$  interaction energies are so strong that they can overwhelm the  $n(\parallel)$ – $\sigma_{\text{P-Cl}}$  repulsive destabilization.

These expectation are borne out in the results of our NBO analysis<sup>24b–d</sup> at the HF/6-311+G\*\* level with the B3LYP/6-311+G\*\* geometries. For **3A**, the adduct with  $n(\perp)$  form is more stable than the  $n(\parallel)$  form by  $\delta\Delta E = \Delta E(\perp) - \Delta E(\parallel) = -7.3$  kcal mol<sup>-1</sup>. Decomposition of this energy difference into  $\delta\Delta E_{\text{CT}}$  and  $\delta\Delta E_{\text{NCT}}$  in eq 7 leads to a greater exclusion repulsion destabilization ( $\Delta E_{\text{NCT}} > 0$ ) of  $\delta\Delta E_{\text{NCT}}$  (= -15.5 kcal mol<sup>-1</sup>) for the  $n(\parallel)$  form. The charge-transfer stabilization ( $\Delta E_{\text{CT}} < 0$ ) is also larger ( $\delta\Delta E_{\text{CT}} = +8.2$  kcal mol<sup>-1</sup>) for the  $n(\parallel)$  than the  $n(\perp)$ , but the difference is smaller than that for  $\delta\Delta E_{\text{NCT}}$ . Thus, despite the larger charge-transfer stabilization with  $n(\parallel)$  than  $n(\perp)$  form, even greater destabilization caused mainly by the exclusion repulsion with  $n(\parallel)$  form results in the overall stability of the  $n(\perp)$  relative to  $n(\parallel)$  adduct for **3A**. In contrast, the overall stability of the  $n(\parallel)$  relative to the adduct for **4A** (by 5.2 kcal mol<sup>-1</sup>) is due to the greater charge-transfer stabilization ( $\delta\Delta E_{\text{CT}} = 25.9$  kcal mol<sup>-1</sup>) with smaller repulsive interaction ( $\delta\Delta E_{\text{NCT}} = -20.7$  kcal mol<sup>-1</sup>) for the  $n(\parallel)$  than  $n(\perp)$  form. Both the  $n_{\text{O}}-\sigma_{\text{P-Cl}}^*$  (-36.2 kcal mol<sup>-1</sup>) and the overall charge transfer (-106.7 kcal mol<sup>-1</sup>) stabilization for Y = Cl are greater than  $n_{\text{O}}-\sigma_{\text{P-F}}^*$  (-28.5 kcal mol<sup>-1</sup>) and the overall delocalization (-87.8 kcal mol<sup>-1</sup>) stabilization for Y = F in the  $n(\parallel)$  forms. This is, of course, the narrower energy gap  $\Delta\epsilon = \epsilon_{\sigma^*} - \epsilon_n$  with Y = Cl than with Y = F in eq 6, which in turn is primarily due to the lower  $\sigma_{\text{P-Cl}}^*$  than  $\sigma_{\text{P-F}}^*$  level (Table 4).

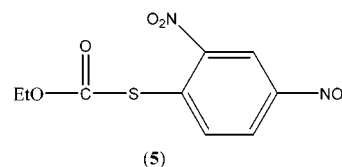
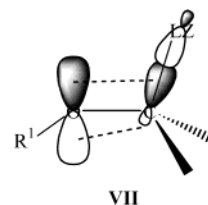
These model system analyses show that: (i) The p lone pair on the atom directly attached to the central P atom has important stabilizing effect on the TBP-5C structure with P–Y apical bond where Y is an electronegative atom. (ii) The lower the  $\sigma_{\text{P-Y}}^*$  orbital, the greater is the stability of  $n(\parallel)$  form, and hence the greater is the apicophilicity of Y.

In the TBP-5C adduct of aryl bis(4-methoxyphenyl) phosphates, **1**, the orientations of lone pairs (p-type) on the two directly bonded oxygens are most probably parallel with the two apical bonds of phosphorus (**VI**)

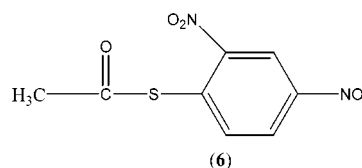
leading to relatively strong  $n_{\text{O}}-\sigma_{\text{ap}}^*$  proximate charge-transfer interactions.<sup>24</sup> As a result of this charge transfer



from the lone pairs to the apical  $\sigma^*$  bonds, the two apical bonds are stretched and weakened so that apical bond cleavage is facilitated. The apical bond to the attacking nucleophile should also be weaker than the corresponding equatorial bond. Thus, in the ap(NX)–ap(LZ) direct attack processes, the magnitudes of  $\rho_{\text{Z}}$  (and  $\beta_{\text{Z}}$ ) and  $\rho_{\text{XZ}}$  values will be small due to long distances involved in the apical bonds of the TBP-5C type TS. This is quite similar to the enhanced leaving group expulsion from of the tetrahedral intermediate (**VII**) by an alkoxy (OR) or phenoxy (OPh) ligand, as time and again pointed out by Castro et al.<sup>16b,27</sup> qualitatively, in the nucleophilic carbonyl substitution reactions. For example, Castro et al.<sup>12e</sup> observed that the aminolysis of *S*-(2,4-dinitrophenyl) *O*-ethyl carbonate (**5**) with secondary alicyclic amines proceeds by a concerted mechanism with  $\beta_{\text{X}} = 0.56$ , whereas *S*-(2,4-dinitrophenyl) acetate (**6**) reacts by a stepwise mechanism with  $\beta_{\text{X}} = 0.8$ –1.0.



(5)



(6)

In the putative tetrahedral intermediate ( $\text{T}^\ddagger$ ) that may be formed in the aminolysis reactions of **5**, the leaving ability becomes so strong due to weakening of the C–LZ bond that the intermediate cannot exist and the reaction proceeds by a concerted path. This enhanced leaving ability in the tetrahedral adduct with **5** compared to that with **6** should result from  $n_{\text{O}}-\sigma_{\text{C-S}}^*$  type proximate charge-transfer interaction (**VII**).<sup>24</sup> The  $n_{\text{O}}-\sigma_{\text{C-LZ}}^*$  type interaction should be the greater, the higher the lone pair  $n$  (or bonding orbital,  $\sigma$ ) energy level and the lower the

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**Table 5. Activation Parameters<sup>a</sup> for the Reactions of Z-Aryl Bis(4-methoxyphenyl) Phosphates with X-Pyridines in Acetonitrile**

Z	X	T <sup>o</sup> C	k <sub>2</sub> × 10 <sup>4</sup> (M <sup>-1</sup> s <sup>-1</sup> )	ΔH <sup>‡</sup> (kcal mol <sup>-1</sup> )	-ΔS <sup>‡</sup> (cal mol <sup>-1</sup> K <sup>-1</sup> )
4-Cl	4-CH <sub>3</sub>	45	14.4	9.4 ± 0.2 <sup>b</sup>	33 ± 1 <sup>c</sup>
		55	24.0		
		65	37.0		
4-CN	H	45	5.90	6.6 ± 0.2	43 ± 1
		55	8.55		
		65	11.7		
4-NO <sub>2</sub>	3-Cl	45	2.67	1.3 ± 0.2	62 ± 1
		55	2.88		
		65	3.20		

<sup>a</sup> Calculated by Eyring equation. <sup>b,c</sup> Standard deviation.

C-LZ  $\sigma^*$  level because the denominator in eq 6,  $\Delta\epsilon = \epsilon_{\sigma^*} - \epsilon_{\sigma}$ , decreases. Since the ethyl group in **5** is an electron donor, the lone pair level on ethoxy oxygen is raised,<sup>2b,28</sup> and electron-withdrawing groups on the leaving group (2,4-(NO<sub>2</sub>)<sub>2</sub>) lower the  $\sigma_{C-S}^*$  level<sup>2b,28</sup> leading to a stronger charge transfer by a reduced  $\Delta\epsilon$  in eq 6. In the tetrahedral structure **VII**, however, the overlap between the p-type lone pair on the oxygen and the bond to the leaving group (C-LZ) can be only partial due to the relative orientations within the tetrahedral structure, i.e.,  $F_{\sigma\sigma^*}$  ( $\propto S_{\sigma\sigma^*}$ ) may be small in eq 6. The corresponding overlap in the TBP-5C adduct **VI** is much more efficient with nearly parallel orientations of the p-lone pair to the apical bonds. Therefore a good leaving group, which has low  $\sigma_{P-LZ}^*$  level due to stronger electron-acceptor substituent Z, will have a strong apicophilicity, and is likely to react by a backside attack concerted mechanism with inversion of configuration. In contrast a poorer leaving group with a weaker apicophilicity is more likely to occupy an equatorial site in the TBP-5C adduct and pseudorotates to an apical site before bond cleavage.

Activation parameters,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , were determined for 3 cases as shown in Table 5. The activation enthalpies are relatively low, especially for the reactions with good leaving groups, Z = 4-CN and 4-NO<sub>2</sub>. For these two reactions, the leaving group departure seems very facile and has progressed to a large extent in the TS as low enthalpies of activation and large negative entropies of activation suggest.

### Conclusion

The rates of the pyridinolysis of Z-aryl bis(4-methoxyphenyl) phosphates in acetonitrile show a biphasic dependence on the basicity of the pyridine nucleophiles. The Brønsted coefficient  $\beta_X$  ( $\beta_{nuc}$ ) changes from a large ( $\beta_X = 0.22-0.39$ ) to a small ( $\beta_X = 0.09-0.14$ ) value as the basicity of pyridine increases. The magnitude of the Brønsted coefficient  $\beta_Z$  ( $\beta_{lg}$ ) shows also similar changes from a large ( $\beta_Z = -0.42$  to  $-0.56$ ) to a small value ( $\beta_Z = -0.08$  to  $-0.28$ ) for the poorer leaving groups (Z = 4-Cl, 3-CN). These results are interpreted to indicate a mechanistic change from a concerted for the weakly basic nucleophiles (X = 3-Cl, 4-CN) to a stepwise mechanism with rate-limiting formation of the TBP-5C transition state for the strongly basic nucleophiles (X = 4-NH<sub>2</sub>, 3-CH<sub>3</sub>). The sign change of the cross-interaction constants,  $\rho_{XZ}$ , supports the proposed mechanistic change

from a concerted ( $\rho_{XZ} = -1.98$ ) to a stepwise ( $\rho_{XZ} = +0.97$ ) process as the basicity of nucleophile becomes stronger. The magnitude of Brønsted  $\beta_Z$  ( $\beta_{lg}$ ) values for the better leaving groups (Z=3-CN, 4-NO<sub>2</sub>) are unusually low ( $\beta_Z = -0.01$  to  $-0.03$ ) suggesting involvement of a direct backside attack TS in which both the nucleophile (NX) and leaving group (LZ) occupy apical sites (ap(NX)-ap(LZ)). The putative TBP-5C adduct leads to a concerted mechanism due to strong proximate charge transfer interactions between the p-lone pair on the equatorially bonded oxygen and the apical bond, ( $n_O(eq)-\sigma^*(ap)$ ). These are supported by the results of NBO analyses at the NBO-HF/6-311+G\*\*//B3LYP/6-311+G\*\* level of theory.

### Experimental Section

**Materials.** Aryl bis(4-methoxyphenyl)phosphates were prepared by following two steps. In step 1, bis(4-methoxyphenyl)chlorophosphate was prepared by reacting phosphorus oxychloride with 4-methoxyphenol for 2 h in the presence of triethylamine in methylene chloride on an ice bath.<sup>29a</sup> Triethylamine hydrochloride salt was separated by filtration. The remaining product was treated with ether and water for workup. After workup, anhydrous MgSO<sub>4</sub> was added, and the solvent was evaporated under reduced pressure after filtration. Bis(4-methoxyphenyl) chlorophosphate was identified by TLC, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC-MS analysis. In step 2, aryl bis(4-methoxyphenyl) phosphates were synthesized by reacting bis(4-methoxyphenyl)chlorophosphate with phenols in the presence of triethylamine in methylene chloride. The substrates were isolated in the similar way described in step 1 and were identified by TLC, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC-MS analysis. All other materials were as described previously.<sup>29</sup> Aldrich GR Grade pyridines were used without purification. The physical constants after column chromatography (silica gel/ethyl acetate + *n*-hexane) were as follows:

**Bis(4-methoxyphenyl) chloro phosphate:** liquid;  $\delta_H$  (CDCl<sub>3</sub>) 6.8–7.3 (bis-4-CH<sub>3</sub>OC<sub>12</sub>H<sub>8</sub>-H, 8H, m), 3.8 (OCH<sub>3</sub>-H, 3H, s);  $\delta_C$  (CDCl<sub>3</sub>) 113–120 (C=C, aromatic), 54 (OCH<sub>3</sub>);  $\nu_{max}$  (neat) 3073 (C-H, aromatic), 2838 (C-H, aliphatic), 1598, 1506, 1465, 1255 (POC<sub>6</sub>H<sub>4</sub>), 1312 (P=O); *m/z* 329 (M<sup>+</sup>).

**4-Chlorophenyl bis(4-methoxyphenyl) phosphate:** liquid;  $\delta_H$  (CDCl<sub>3</sub>) 7.0–7.1 (bis-4-OCH<sub>3</sub>C<sub>12</sub>H<sub>8</sub>-H + 4-ClC<sub>6</sub>H<sub>4</sub>-H, 12H, m), 3.8 (OCH<sub>3</sub>, 3H, s);  $\delta_C$  (CDCl<sub>3</sub>) 113–128 (C=C, aromatic), 54 (OCH<sub>3</sub>);  $\nu_{max}$  (neat), 3070 (CH, aromatic), 2839 (CH, aliphatic), 1598, 1501, 1254, 1184 (POC<sub>6</sub>H<sub>4</sub>), 1308 (P=O); *m/z* 421 (M<sup>+</sup>).

**3-Chlorophenyl bis(4-methoxyphenyl) phosphate:** liquid;  $\delta_H$  (CDCl<sub>3</sub>) 6.7–7.3 (bis-4-CH<sub>3</sub>OC<sub>12</sub>H<sub>8</sub>-H + 3-ClC<sub>6</sub>H<sub>4</sub>-H, 12H, m), 3.7 (OCH<sub>3</sub>, 3H, s);  $\delta_C$  (CDCl<sub>3</sub>) 113–127 (C=C, aromatic), 54 (OCH<sub>3</sub>);  $\nu_{max}$  (neat) 3072 (CH, aromatic), 2840 (C-H, aliphatic), 1595, 1501, 1254, 1183 (P-O-C<sub>6</sub>H<sub>4</sub>), 1307 (P=O); *m/z* 421 (M<sup>+</sup>).

**3-Cyanophenyl bis(4-methoxyphenyl) phosphate:** Liquid;  $\delta_H$  (CDCl<sub>3</sub>) 6.7–7.5 (bis-4-CH<sub>3</sub>OC<sub>12</sub>H<sub>8</sub>-H + 3-CNC<sub>6</sub>H<sub>4</sub>-H, 12H, m), 3.8 (OCH<sub>3</sub>, 3H, s);  $\delta_C$  (CDCl<sub>3</sub>) 113–119 (C=C, aromatic), 54 (OCH<sub>3</sub>);  $\nu_{max}$  (neat) 3001 (CH, aromatic), 2839 (CH, aliphatic), 2225 (C≡N), 1614, 1503, 1448, 1180 (POC<sub>6</sub>H<sub>4</sub>), 1300 (P=O); *m/z* 412 (M<sup>+</sup>).

**4-Cyanophenyl bis(4-methoxyphenyl) phosphate:** liquid;  $\delta_H$  (CDCl<sub>3</sub>) 6.7–8.0 (bis-4-CH<sub>3</sub>OC<sub>12</sub>H<sub>8</sub>-H + 4-CNC<sub>6</sub>H<sub>4</sub>-H, 12H, m), 3.8 (OCH<sub>3</sub>, 3H, s);  $\delta_C$  (CDCl<sub>3</sub>) 113–132 (C=C, aromatic), 54 (OCH<sub>3</sub>);  $\nu_{max}$  (neat), 3000 (C-H, aromatic), 2838 (C-H, aliphatic), 2227 (C≡N), 1614, 1502, 1447, 1180 (POC<sub>6</sub>H<sub>4</sub>), 1297 (P=O); *m/z* 412 (M<sup>+</sup>).

**4-Nitrophenyl bis(4-methoxyphenyl) phosphate:** liquid;  $\delta_H$  (CDCl<sub>3</sub>) 6.8–8.2 (bis-4-CH<sub>3</sub>OC<sub>12</sub>H<sub>8</sub>-H + 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-H, 12H, m), 3.8 (OCH<sub>3</sub>, 3H, s);  $\delta_C$  (CDCl<sub>3</sub>) 113–124 (C=C, aromatic),

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54 (OCH<sub>3</sub>);  $\nu_{\max}$  3114 (CH, aromatic), 2838 (CH, aliphatic), 1588 and 1347 (NO<sub>2</sub>), 1527, 1506, 1347, 1194 (POC<sub>6</sub>H<sub>4</sub>), 1296 (P=O);  $m/z$  430 (M<sup>+</sup>).

**Kinetic Procedure.** Rates were measured as described previously<sup>6g,29</sup> with a large excess of pyridines: [substrate] =  $1 \times 10^{-3}$  M and [pyridines] = 0.04–0.16 M.

**Product Analysis.** 4-Chlorophenyl bis(4-methoxyphenyl) phosphate was refluxed with excess 4-acetylpyridine for more than 15 half-lives at 55.0 °C in acetonitrile. Acetonitrile was evaporated under reduced pressure, and the product mixture was treated with ether and water for workup; during workup, dilute hydrochloric acid was treated to remove excess 4-acetylpyridine and after workup dried over anhydrous MgSO<sub>4</sub>. The product was isolated by evaporating the solvent under reduced pressure after filtration. The physical constants after column chromatography (silica gel/ethyl acetate + *n*-hexane) were as follows. (4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>P(=O)N<sup>+</sup>C<sub>5</sub>H<sub>4</sub>-4-COCH<sub>3</sub>: liquid;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 6.6–7.3 (bis-4-methoxy-C<sub>12</sub>H<sub>8</sub>-H + 4-COCH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>-H, 12H, s), 3.8 (OCH<sub>3</sub>, 3H, s), 1.7 (COCH<sub>3</sub>, 3H, s);  $\nu_{\max}$  (neat) 3076 (CH, aromatic), 2839 (CH, aliphatic), 1872 (CH<sub>3</sub>CO), 1727 (CO), 1588, 1502, 1029 (POC<sub>6</sub>H<sub>4</sub>), 1303 (P=O).

**Calculations.** Density functional theory (DFT) calculations were performed with Gaussian 98 system of programs.<sup>30</sup> The DFT method is particularly useful for calculations involving large number of nonhydrogen atoms at the correlated level. The B3LYP hybrid exchange-correlation functionals are known to give good equilibrium geometries, vibrational frequencies and accurate molecular atomization energies.<sup>31</sup> Geometries were optimized at the B3LYP/6-311+G\*\* level of theory. To represent lone pair orbitals and second row elements (P, Cl) (also H) properly a diffuse function (+) and polarization functions (\*\*) were used, respectively. Equilibrium structures

were confirmed by calculations of vibrational frequencies. The natural bond orbital (NBO) analyses<sup>24b-d</sup> were carried out to obtain proximate bond–antibond ( $\sigma$ – $\sigma^*$ ) orbital interaction energies at the HF/6-311+G\*\* level.

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**Supporting Information Available:** The calculated electronic energies and Z-matrixes of **2**, **2A**-axial, **2A**-equatorial, **3**, **3A**-axial, **3A**-equatorial, **4**, **4A**-axial, and **4A**-equatorial. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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