Stereoelectronic Effects on the One-Electron Donor Reactivity of Trivalent Phosphorus Compounds. Experimental and Theoretical Investigations

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Peak oxidation potentials E_p^{ox} of acyclic and cyclic phosphinites, phosphonites, and phosphites were measured by cyclic voltammetry. The inductive effect of the ligands attached to the phosphorus is a primary factor to determine E_p^{ox} of these compounds. The geometry of the compound is another important factor; E_p^{ox} is lowered when the compound adopts a geometry in which the phosphorus lone-pair orbital overlaps with the adjacent oxygen p-orbital. The stereoelectronic effects found here are interpreted in terms of the energy level of the highest occupied molecular orbital (HOMO) of these phosphorus compounds.

Trivalent phosphorus compounds Z_3P are good nucleophiles. That is, Z_3P undergoes ionic reaction with an electrophile, in which Z_3P acts formally as a two-electron donor. Such reactivity of Z_3P has been investigated comprehensively. Meanwhile, the behavior of Z_3P as one-electron donor has recently been acknowledged.[1—4] When treated with a suitable one-electron acceptor, Z_3P releases an electron to generate the radical cation $Z_3P^{\bullet+}$. There has been no study on what factors determine the one-electron donor reactivity of Z_3P.

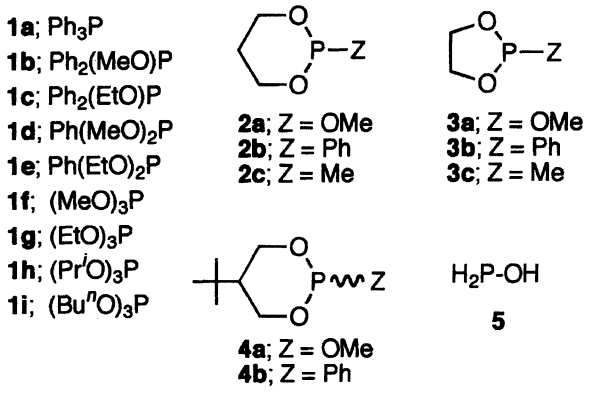
The "two-electron donor" reactivity of Z_3P is affected by α-oxygens attached to the phosphorus. For example, stereoelectronic effects on basicity and nucleophilicity of phosphites have been investigated on theoretical and experimental bases.[5—7] Then, it occurs to us that stereoelectronic effects might be operative also in determining the one-electron donor reactivity of Z_3P.

The reactivity of a given compound as a one-electron donor is represented by its oxidation potential E_p^{ox}. Then, in order to find such dependence of one-electron donor reactivity of Z_3P on its electronic structure and its geometry, we carried out cyclic voltammetry on several acyclic and cyclic trivalent phosphorus compounds, each of which has one or more P–O bonds. Comparison of E_p^{ox} values of these compounds shows that one-electron donor reactivity of Z_3P is determined not only by "through-bond" inductive effects of the α-oxygens but also by "through-space" stereoelectronic effects of the lone-pairs of these oxygens. The observations are rationalized on theoretical bases with ab initio calculations. Thus, the overlap of the phosphorus lone-pair with the oxygen p-orbital in a given trivalent phosphorus compound makes its HOMO energy level higher, which facilitates one-electron transfer from the compound.

Results

Cyclic Voltammetry. Cyclic voltammetry of acyclic compounds, **1a—i** ($(0.5—1.0)\times10^{-2}$ M, 1 M=1 mol dm^{-3}), and cyclic compounds, **2a—b** and **3a—b** ($(1.0—5.0)\times10^{-2}$ M), was carried out at room temperature with a scan rate of 50 mV s^{-1} in acetonitrile (Scheme 1). As represented in Fig. 1 for selected compounds, each voltammogram exhibited an oxidation wave that was principally reversible. A slight decrease in the peak current was observed upon repeated scans, indicating that the radical cation $Z_3P^{\bullet+}$, the oxidized form of Z_3P, partially decomposes by reacting with a trace of water in the solvent.[8] Peak oxidation potentials E_p^{ox} determined are summarized in Table 1.

Cyclic voltammetry of 2-phenyl-1,3,2-dioxaphosphorinane (**2b**) was carried out also at −10, −20, and −30 °C,



Scheme 1.

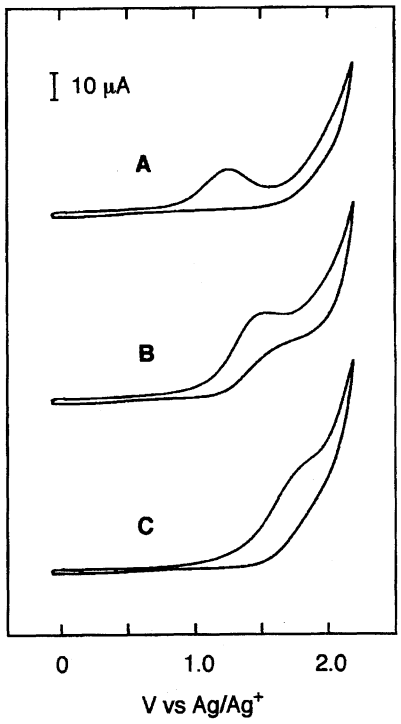


Fig. 1. Cyclic voltammograms of **1c** (A), **1e** (B), and **1g** (C) in CH_3CN (0.10 M Et_4NBF_4).

Table 1. Peak Oxidation Potentials of Trivalent Phosphorus Compounds

Z_3P	E_p^{ox} (V)[a]
1a	0.94
1b	1.24
1c	1.20
1d	1.52
1e	1.48
1f	1.84
1g	1.90
1h	1.86
1i	1.88
2a	2.04
2b	1.38
3a	>2.50
3b	2.33
trans-**4a**[b]	2.18
cis-**4a**[c]	>2.50
trans-**4b**[b]	1.48
cis-**4b**[c]	>2.50

a) Peak potential vs. Ag/Ag^+. Determined in acetonitrile using Et_4NBF_4 (0.10 M) as supporting electrolyte. b) Measured immediately after the preparation of the material. c) Measured after four days.

which showed that the oxidation peak becomes smaller as the temperature is lowered (Fig. 2).

Examinations Using Cyclic Compounds with Fixed Geometry. A cyclic compound with fixed geometry, 5-*t*-butyl-2-methoxy-1,3,2-dioxaphosphorinane (**4a**), was prepared via condensation of the cyclic phosphorochloridite Z_2P–Cl with methanol (Eq. 1).

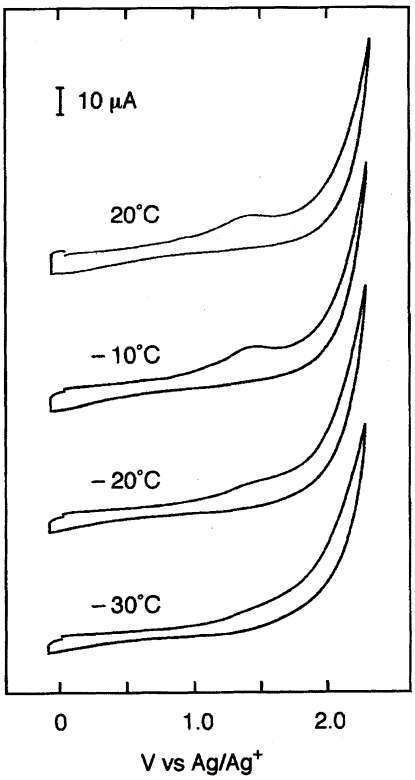
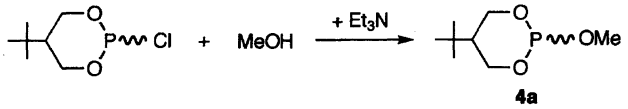
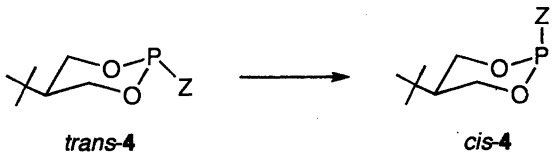


Fig. 2. Cyclic voltammograms of **2b** in CH_3CN (0.10 M Et_4NBF_4) recorded at 20 °C, −10 °C, −20 °C, and −30 °C.



(1)

It has been shown[9] that this method of preparation initially affords a considerable amount of the thermodynamically less stable *trans*-isomer, in which both *t*-butyl and methoxy groups are equatorial, and this isomer gradually isomerizes to the more stable *cis*-isomer through configurational inversion at the phosphorus (Eq. 2).[10]



(2)

In fact, we observed two peaks on GC from the material immediately after the preparation. The area ratio of these peaks at this stage was 65/35 and then dropped to 4/96 after four days (Table 2). To eliminate the possibility of the isomerization of **4a** at the GC injector port, the material was treated with sulfur powder (S_8) in benzene and analyzed on GC or GCMS at the initial and at the final stages, respectively; the oxidation of trivalent phosphorus compounds with S_8 is known to take place with complete retention of stereochemistry.[11] At each stage, two peaks resulting from the two isomers of the corresponding thiophosphate were detected in

Table 2. Isomerization of **4**

Z_3P		*trans*/*cis*[a]		
		GC	GC of Z_3P=S	^{1}H NMR
4a	Initial	65/35	61/39	—
	After 4 d[b]	4/96	3/97	5/95
4b	Initial	—[c]	18/82	—
	After 4 d[b]	—[c]	14/86	—

a) Ratio of *trans*- and *cis*-isomers. No correction was made based on sensitivity differences. b) Kept in a refrigerator. c) *Trans*-**4b** and *cis*-**4b** were not separable on GC.

the area ratio that was nearly the same as that observed for **4a** (Table 2). Furthermore, ^{1}H NMR spectrum of **4a** recorded at the final stage gave two signals assignable to *t*-butyl protons in the ratio of 5/95 (Table 2), a larger and a smaller signal resonating at 0.87 and 1.01 ppm, respectively. Based on the reported values of the chemical shift,[9] the major isomer at the final stage is identified to be *cis*-**4a**. The findings above indicate clearly that the material consists of *trans*-**4a** and *cis*-**4a** in comparable amounts at the initial stage, and it becomes highly cis rich at the final stage.

Cyclic voltammetry was carried out on **4a** (8.0×10^{-2} M in CH_3CN) immediately after the preparation of the material and after four days, respectively. The voltammogram obtained at the initial stage gave a small but distinct oxidation peak at 2.18 V (voltammogram **A** in Fig. 3), while the peak was hardly observed at the final stage (**B** in Fig. 3). Keeping the behavior in the isomerization of **4a** in mind, we conclude that the oxidation peak initially observed arises from *trans*-**4a**, and that *cis*-**4a** has an oxidation potential higher than the upper limit measurable on our instrument (2.5 V).

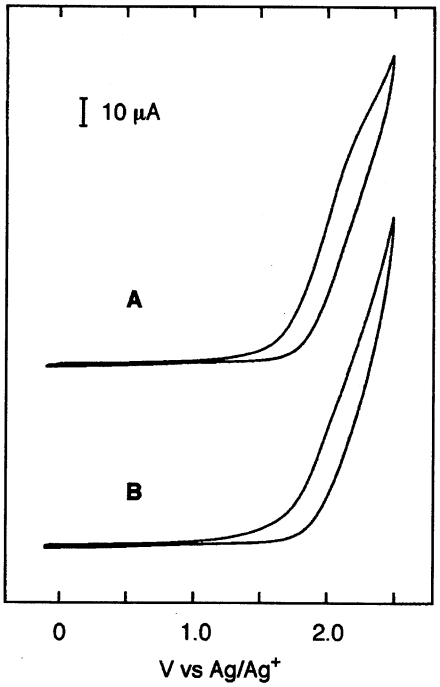
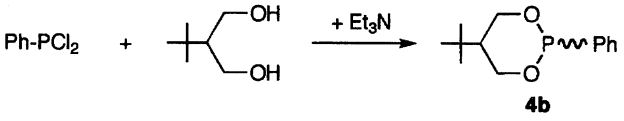


Fig. 3. Cyclic voltammograms of **4a** in CH_3CN (0.10 M $Et_4NBF_4^-$) recorded immediately after the preparation of the material (A) and after 4 d (B).

5-*t*-Butyl-2-phenyl-1,3,2-dioxaphosphorinane (**4b**) also was synthesized via cyclization of dichlorophenylphosphine with 2-*t*-butyl-1,3-propanediol (Eq. 3).



(3)

Trans-**4b** and *cis*-**4b** were not separable on GC, so the material was treated with S_8 immediately after the preparation and after four days, respectively. The isomer ratio of the resulting thiophosphonate was analyzed on GC or GCMS, which showed, as has been reported,[12] that *trans*- and *cis*-isomers of **4b** are already in the equilibrium ratio (cis rich) at the initial stage. Meanwhile, cyclic voltammetry of **4b** was carried out at the initial and the final stages. The voltammogram obtained at each stage gave an oxidation peak at 1.48 V as a shoulder. The peak with this small current probably arises from *trans*-**4b** that exists in a small amount, while the oxidation potential for the major isomer, *cis*-**4b**, is higher than 2.5 V.

Assignments of oxidation peaks for the cyclic compounds **4a** and **4b** are shown in Table 1.

Discussion

To examine inductive effects of the ligands Z in trivalent phosphorus compounds Z_3P on their oxidation potentials, E_p^{ox} is plotted against $\sum\sigma^*$, the sum of the Taft's substituent constants σ^* of Z (Fig. 4). The σ^* scale is chosen as a parameter group representing inductive effects of Z simply because of its availability from the literature,[13–15] so its use is somewhat arbitrary. However, a tendency is obvious in Fig. 4 that E_p^{ox} becomes larger with increasing $\sum\sigma^*$, which shows clearly that the electron transfer from the compound becomes more difficult as the ligand becomes more electron-

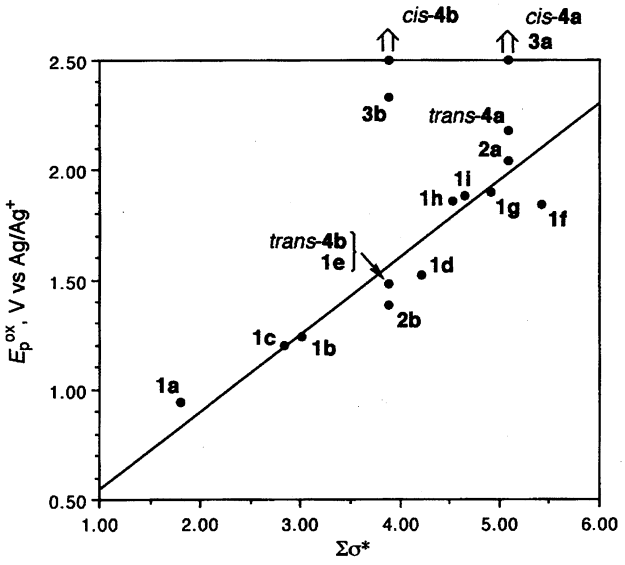


Fig. 4. Plot of E_p^{ox} vs. $\sum\sigma^*$.

withdrawing. This is to be expected; the same tendency has been found between E_p^{ox} of triarylphosphines and the sum of σ^+ of the ring substituents.[16]

A more important finding in Fig. 4 is that the points for the compounds with a six-membered ring, 2-methoxy- (**2a**) and 2-phenyl-1,3,2-dioxaphosphorinane (**2b**), fall on the correlation line made by acyclic compounds **1**, whereas the points for the compounds with a five-membered ring, 2-methoxy- (**3a**) and 2-phenyl-1,3,2-dioxaphospholane (**3b**), are significantly deviated upward. Apparently, the difference in oxidation potentials between **2** and **3** results from the difference in the conformations of these compounds.

To find the origin of the conformational effects on E_p^{ox}, we compare the oxidation potentials of **1**—**3** with those of 5-*t*-butyl substituted phosphorinanes **4**, the compounds that have fixed conformations. *Trans*-**4a** and *trans*-**4b**, respectively, exhibit E_p^{ox} values similar to those of the corresponding acyclic compounds **1** or the cyclic compounds without 5-*t*-butyl **2** (Fig. 4). With respect to the geometry around the P–O bond, the trans isomers of **4** belong to the same category as the compounds **1** and **2**. That is, in *trans*-**4**, the phosphorus lone-pair orbital is fixed to be axial so that it almost overlaps with the adjacent ring oxygen p-orbital (**I**;R=Bu^t in Chart 1). Obviously, **2** can adopt the same chair conformation (**I**; R=H). In addition, **1** can take a conformation in which the phosphorus lone-pair orbital overlaps with the oxygen p-orbital, since free-rotation is allowed around the P–O bond in **1**. On the other hand, such a conformation is not possible for *cis*-**4a**, *cis*-**4b**, and **3**, the compounds whose E_p^{ox} values are much higher than those of **1**, **2**, and *trans*-**4**. Thus, the *cis* isomers of **4** have a fixed conformation in which the phosphorus lone-pair orbital is nearly perpendicular to the ring oxygen p-orbital (**II**; R=Bu^t). In compounds **3**, these orbitals are forced to take orientations gauche to each other (**III**).

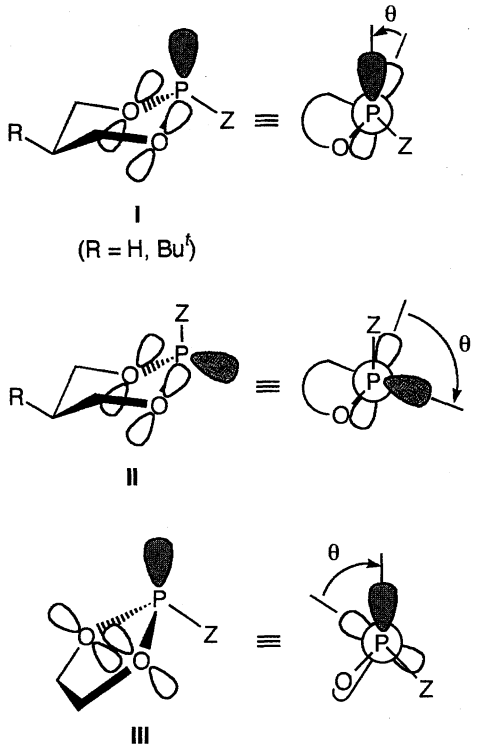


Chart 1.

Based on considerations above, we conclude that one-electron transfer from a trivalent phosphorus compound is facilitated by the overlap of the phosphorus lone-pair orbital with the oxygen p-orbital.

In accordance with the conclusion is the fact that the oxidation peak of **2b** at 1.38 V almost disappears below −20 °C (Fig. 2). For cyclic compounds **2**, conformer **I** is thermodynamically less stable than conformer **II**.[17] There is rapid equilibrium between **I** and **II** by chair–chair interconversion at room temperature (Eq. 4),[12] and **I** is sufficiently supplied within the CV time scale.

(4)

As a result, the oxidation peak resulting from one-electron transfer from **I**, the analog of *trans*-**4**, is observed at room temperature, the observed E_p^{ox} values of **2** being similar to the corresponding trans isomers of **4**. At lower temperatures, however, the equilibrium is "frozen", so the one-electron transfer occurs preferentially from conformer **II**, the analog of *cis*-**4**.[18] Since **II** certainly has an oxidation potential higher than 2.5 V, the cyclic voltammograms recorded for **2b** at lower temperatures give no oxidation peak on our instrument.

More quantitative formulation is allowed by estimating p_z–O–P–Lp dihedral angle θ between the lobes of the phosphorus lone-pair and the adjacent oxygen p-orbital. Thus, ab initio calculations were carried out to obtain the optimized structures of two conformers of **2a** (**I** and **II**; R=H, Z=OMe) as well as **3a** (**III**; Z=OMe). In each structure, p_z–O–P–Lp dihedral angle θ was estimated. Calculations were carried out also for the corresponding model compounds **2c** and **3c** (**I**, **II**, and **III**; R=H, Z=Me), to estimate θ. As shown in Table 3, for each series, the absolute value of θ increases in the order of **I**<**III**<**II**,[19] which is parallel to the increasing order of the peak oxidation potentials within series of cyclic compounds with the same ligands (e.g., in a series of cyclic phosphonates, *trans*-**4b**<**3b**<*cis*−**4b**). Thus, one-electron transfer from a trivalent phosphorus compound becomes more facile as the

Table 3. p_z–O–P–Lp Dihedral Angle θ of Cyclic Trivalent Phosphorus Compound

 X	p_z–O–P–Lp θ (deg.)[a]	
	Xa (Z = OMe)	**Xc** (Z = Me)
2 in **I**[b]	−14	−16
2 in **II**[c]	82	78
3	67	62

a) Estimated for the structures optimized by ab initio calculations. For definition of signs, see the Newman projection formulas in Chart 1. b) Conformer **I**. c) Conformer **II**.

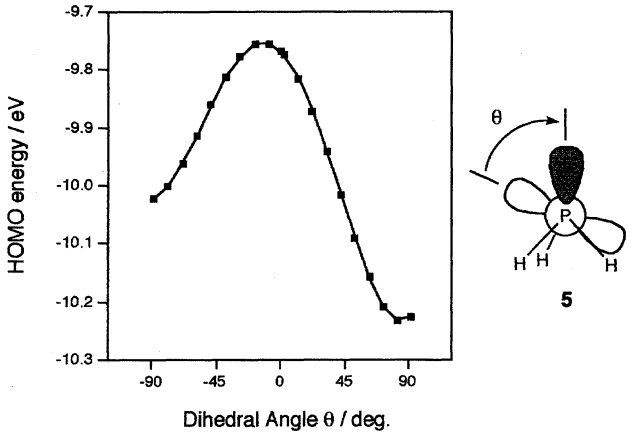


Fig. 5. HOMO energy of **5** as a function of p_z–O–P–Lp dihedral angle θ.

overlap between the phosphorus lone-pair and the oxygen p-orbital becomes larger.

In order to discuss the stereoelectronic effects on E_p^{ox} quantitatively, ab initio calculation was performed with RHF/6-31G(d) on a model compound, phosphinic acid **5**. Thus the energy level of the highest occupied molecular orbital (HOMO) of **5** was obtained as a function of p_z–O–P–Lp dihedral angle θ. Figure 5 shows that the geometry with dihedral angle $\theta=-10°$ is the maximum in the HOMO energy, whereas the geometry with $\theta=80°$ is the minimum. This result of the calculation predicts that the compound in which the phosphorus lone-pair nearly overlaps with the oxygen p-orbital releases an electron most easily, and the compound with these lone-pairs being nearly perpendicular to each other is the least reactive in one-electron transfer. This is exactly what we observed in the present study. Thus, the stereoelectronic effects found experimentally are well accounted for in terms of the HOMO energy level of the compound.

Experimental and theoretical studies on oxidation potentials of silicon-substituted ethers[20] and catechol derivatives[21] have been presented. The studies have indeed shown that the higher the HOMO energy, the lower the oxidation potential of the compound. Our present study provides another example for such a relationship between the oxidation potential of a given reductant and its HOMO energy level.

The stereoelectronic effects on one-electron donor reactivity of trivalent phosphorus compounds are parallel to the stereoelectronic effects on two-electron donor reactivity such as nucleophilicity or basicity of these phosphorus compounds.[5—7] That is, overlap of the phosphorus lone-pair with the adjacent α-oxygen p-orbital enhances nucleophilic reactivity of trivalent phosphorus compounds. Such effects, which are often termed "α-effect", also are explainable in the term of interaction between α-oxygen p-orbital and the phosphorus lone-pair in a ground-state, which raises the HOMO energy level to destabilize the ground state.[7] Thus, the origin of the stereoelectronic effects on one-electron reactivity is the same as that of the stereoelectronic effects on two-electron donor reactivity, which shows that one-electron transfer occurs from the phosphorus lone-pair.[6]

Experimental

Instruments. Cyclic voltammetry was carried out on a Cypress Systems OMNI 90 potentiostat using a platinum and Ag/Ag^+ electrode as a working and a reference electrode, respectively, and using tetraethylammonium tetrafluoroborate (0.10 M) as supporting electrolyte. GC analysis was performed on a Shimadzu GC 14A gas chromatograph. Mass spectra were obtained on a Shimadzu GCMS-QP2000A gas chromatograph-mass spectrometer equipped with a Shimadzu GC-MSPAC 200S data processor. ^{1}H NMR spectra were obtained on a Varian XL 200 NMR spectrometer.

Materials. Triphenylphosphine **1a** (Tokyo Chemical Industry), phosphinites **1b—c**, phosphonites **1d—e** (Aldrich), and phosphites **1f—i** (Tokyo Chemical Industry) were commercially available. Cyclic compounds **2—4** were prepared according to the method reported previously,[1c] and purified through distillation or flash-chromatography on silica gel with ethyl acetate as eluent.

Ab Initio Calculations. The optimized structures of cyclic compounds **2** and **3** were obtained by the Gaussian[22] 94 program at RHF/6-31G(d) level. A model compound H_2POH (**5**) was optimized at a certain H–O–P–H dihedral angle by applying the GAMESS[23] programs, for which the HOMO energy level was calculated at RHF/6-31G(d) level. With repeated calculations with changing H–O–P–H dihedral angle, the HOMO energy level of **5** was obtained as a function of the p_z–O–P–Lp dihedral angle.

Computation time of Gaussian 94 was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University. One of the authors (S.Y.) acknowledges the financial support of a Tezukayama Research Grant in 1997.

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the conformer with 5-*t*-butyl being axial contributes very little, if any.

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