ciation to Toshiba Silicon Co., Ltd., and Shin-etsu Chemical Co., Ltd., for a gift of organochlorosilanes.

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Hydroxyphosphoranes and Phosphoranoxide Anions—Synthesis, Reactivity, and Acidity of Pentacoordinate Phosphorus Acids

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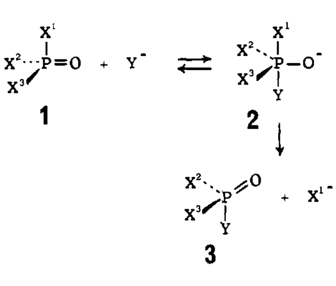
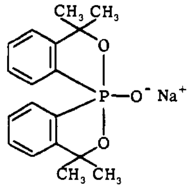
Abstract: The reaction between phosphorus oxychloride and bifunctional alkoxy Grignard reagents gives stable pentacoordinate magnesium phosphoranoxides, such as **9**. The less basic of these, the fluoro-substituted anion of **9**, is not protonated by aqueous ammonium chloride and is isolated as a crystalline salt. Protonation of the phosphoranoxide anions of **4** and **9** gives hydroxyphosphoranes **6** and **10**. While **6** equilibrates in solution with its open-chain tautomer **7**, only the hydroxyphosphorane structure is detected for **10**. Sodium phosphoranoxide **4** reacts with methyl iodide, giving the methoxyphosphorane **20**. Trifluoromethanesulfonic acid reacts with **6** or with olefin **12** to give the stable spirocyclic dioxyphosphonium salt **17**. The analogous reaction between **10** and this acid yields a complex mixture of products. Phosphonium salt **17** and Grignard reagents give dioxyphosphoranes **18** and **19**. The pK_a of **6** is estimated to be in the range 10–11, while the more acidic **10** has a pK_a of 5.3 ± 0.2.

Hydroxyphosphoranes and their conjugate bases, phosphoranoxide anions **2**, are commonly accepted as intermediates or transition states in nucleophilic displacements at the tetracoordinate phosphorus of compounds containing P═O bonds.[2] Recently, acid-catalyzed[3] or thermal[4] conversions of tetrahedral phosphine oxides into exceptionally stable pentacoordinate trigonal bipyramidal (TBP) oxyphosphoranes have been observed. This has paved the way for the synthesis of a thermally stable hydroxyphosphorane.[5] Trapping unstable hydroxyphosphoranes[6] and spectroscopic evidence[7] for equilibrium between a hydroxy phosphate and a hydroxyphosphorane in solution have also been reported. None of these hydroxyphosphoranes, all containing five-membered ring alkoxy or carboxy ligands, gave stable metal phosphoranoxides. In every case, deprotonation of the pentacoordinate phosphorus species led to tetra- or hexacoordinate species.[5,7]

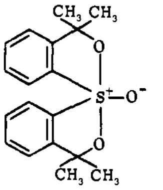


Treatments of some hydroxyphosphoranes with amines have been reported[8,9] to yield crystalline complexes. The spectral data[8,9] are not, however, consistent with deprotonation of the hydroxyphosphoranes to form salts, as we shall establish in this paper.

Earlier studies in this laboratory, centered on tetracoordinate TBP sulfuranes[10,11] and pentacoordinate sulfurane oxides, suggested to us that the phosphoranoxide anion of **4**, isoelectronic with stable sulfurane oxide **5**, might be isolable. This proved possible.[12] We now report further studies, including the preparation and some properties of a new, very stable hydroxyphosphorane, **10**. Acidities and reactivities of two compounds containing this new functional group, pentacoordinate phosphorus hydroxy acids, are discussed.



4, $\delta_{^{31}P}$ -26.9



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Results and Discussion

Synthesis and Structure. In a recent communication[12] we

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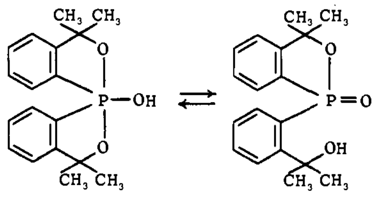
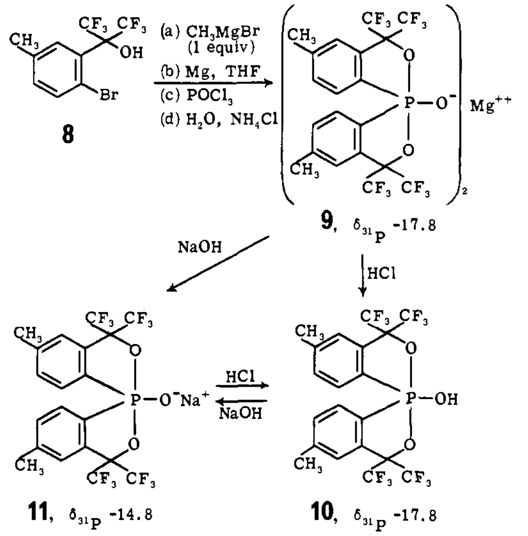
have described the preparation of the sodium phosphoranoxide **4** from the hydroxyphosphorane **6** and sodium hydride in tetrahydrofuran (THF). This salt was also produced from **6** and sodium methoxide in methanol, though over 3 equiv of the base was required to completely deprotonate the weakly acidic **6**. In solution, **6** equilibrates with its open-chain tautomer **7**, as shown by variable-temperature ^{31}P NMR.[12] The proportion of **6** is increased with the bacisity of the solvent (upon going from CDCl$_3$ to C$_5$D$_5$N) and with decreasing temperature.[12] The preparation of **6** from phosphorus oxychloride and the Grignard reagent prepared from 1-methyl-1-(2-bromophenyl)ethanol allows direct observation of the intermediate magnesium derivative of **4**.[12] The synthesis of **6** is analogous to that of **10**, outlined in Scheme I, except that **4** is completely protonated by aqueous ammonium chloride.

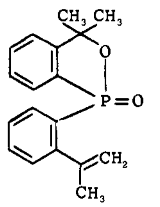

6, $\delta_{^{31}P}$ -26.3 (CH$_3$OD at -10 °C)
7, $\delta_{^{31}P}$ 53.7 (CH$_3$OD at -10 °C)

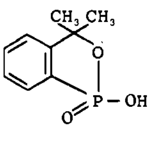
In our preliminary account[12] we reported the use of magnesium powder for the preparation of **6**. We have found that ordinary magnesium turnings are as effective as the powder in the synthesis of both **6** and **10**. Conversely, the reaction of 2 equiv of *n*-butyllithium and 1-methyl-1-(2-bromophenyl)ethanol, followed by reaction with 0.5 equiv of phosphorus oxychloride, results in a very poor yield of **6**. The major phosphorus-containing product isolated from this reaction is olefin phosphinate **12**. Two volatile products are also isolated and identified as styrene and *o*-chlorostyrene. The possible origin of **12** from the reaction of **6** with *n*-butyllithium is supported by the observation that reaction of equimolar amounts of these reagents in THF yields a ca. 1:1 mixture of **12** and the lithium derivative of **4**. Other routes to **12**, not involving **6** as an intermediate, can also be invoked. No evidence is seen[14] for potassium hydroxide catalysis of the analogous decomposition of sulfurane oxide **5**. It is interesting to note that **12** is the only pure product which is isolated from the complex mixture obtained from phosphorus trichloride and the Grignard reagent made from 1-methyl-1-(2-bromophenyl)ethanol.[15]

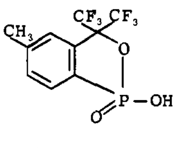
In the syntheses of both **6** and **10** relatively strong acids are isolated as byproducts. These acids, **13** and **14**, are the products of 1:1 reactions of phosphorus oxychloride and the appropriate Grignard reagent.

Scheme I




12, $\delta_{^{31}P}$ 44.2

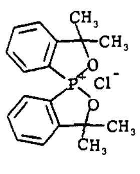

13, $\delta_{^{31}P}$ 39.3

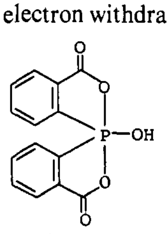

14, $\delta_{^{31}P}$ 31.3

The chiral hydroxyphosphoranes **6** and **10** contain diastereotopic *gem*-dimethyl and *gem*-bis(trifluoromethyl) groups, respectively. These magnetically nonequivalent groups exhibit two methyl singlets (δ 1.74, 1.79) and two CF$_3$ quartets (ϕ 74.72, 75.61, $^4J_{FF}$ = 9 Hz) in the corresponding ^{1}H and ^{19}F NMR spectra of **6** and **10**, respectively. Only one CH$_3$ singlet is observed in the ^{1}H NMR spectrum of **13**, and one CF$_3$ singlet is found in the ^{19}F NMR of **14**. The high-field ^{31}P NMR chemical shifts of **6**, **10**, and the corresponding phosphoranoxide salts are typical of phosphoranes. These are to be contrasted with the relatively low-field ^{31}P NMR values for the tetracoordinate **7**, **12**, **13**, and **14**.

A characteristic feature of the ^{1}H NMR spectra of **6** [δ 8.03 (CDCl$_3$), 8.49 (C$_5$D$_5$N)] and **10** (δ 8.13, $^3J_{HP}$ = 11 Hz) is the low-field resonance of the two aromatic protons ortho to phosphorus in each compound. Earlier studies of sulfuranes,[10,13] and more recent findings with iodinanes[16] and hypervalent silicon compounds,[17] suggest to us that this is reliably indicative of the close proximity of these protons to an apical electronegative atom. This proximity is enforced in a TBP molecule in which the central hypervalent atom is included in an apical-equatorial five-membered ring, as in **6** and **10**. No exceptions to this correlation are observed for the phosphoranes reported here.

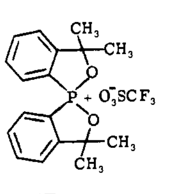
Reactivity. The chemical properties of hydroxyphosphoranes are almost unknown. The only stable hydroxyphosphorane reported[5] prior to this work is destroyed by water and is inert toward thionyl chloride.[9a] Unstable hydroxyphosphoranes have been trapped[6,7c] as methoxyphosphoranes by reaction with CH$_2$N$_2$. Hydroxyphosphoranes **6** and **10** are quite different in their chemical reactivity. The reaction of **6** with thionyl chloride at ambient temperature in CDCl$_3$ produces the spirobicyclic phosphonium chloride **15** ($\delta_{^{31}P}$ 81.8, a chemical shift very similar to that of **17**, $\delta_{^{31}P}$ 82.9). Salt **15** is thermally unstable, undergoing dehydrohalogenation to give **12**. The analogous hydroxyphosphorane **10**, with more strongly electron-withdrawing fluoroalkoxy groups, does not react with thionyl chloride to give a chlorophosphorane. The carboxylate ligands of **16** are also sufficiently electron withdrawing to make **16** similarly unreactive toward thionyl chloride.[9a] It is understandable that electron-withdrawing substituents should make it more difficult to introduce the positive charge of the phosphonium species analogous to **15**.


15, $\delta_{^{31}P}$ 81.8

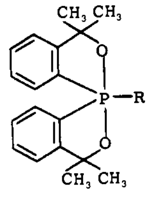

16, $\delta_{^{31}P}$ -38.5

A reaction occurs between trifluoromethanesulfonic (triflic) acid and either olefin **12** or hydroxyphosphorane **6** to give the stable spirobicyclic phosphonium triflate **17**.[15] The protonation of the double bond of **12** may either give a tertiary benzylic cation which subsequently attacks the P=O oxygen or lead in a more concerted manner directly to **17**. The observation that **10** gives a complex mixture of products, rather than a high yield of the corresponding phosphonium triflate, again reflects the high energy of the phosphonium ion with two fluoroalkoxy ligands.

Phosphonium triflate **17** is not hygroscopic, but it is easily hydrolyzed to give **6**. The synthetically useful reactions of **17** include reduction with $LiAlH_4$ and nucleophilic alkylation at phosphorus with Grignard reagents. The $LiAlH_4$ reduction produces the novel tetracoordinate TBP phosphoranide anion,[15] which can be protonated to give a stable P-H phosphorane, or alkylated at phosphorus with electrophiles such as benzyl bromide.[15] Phosphoranes such as **18** and **19** are therefore conveniently prepared either by the reaction of **17** with RMgX or by reaction of the corresponding phosphoranide anion with RX. Earlier syntheses of **18** involved rather lengthy and lower yield procedures.[18]



17, $\delta_{^{31}P}$ 82.9



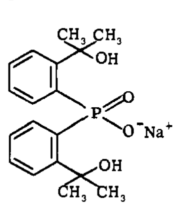
18, R = Ph, $\delta_{^{31}P}$ -44.5
19, R = Me, $\delta_{^{31}P}$ -39.2
20, R = OMe, $\delta_{^{31}P}$ -25.6

Treatment of **17** with 1 equiv of tetrabutylammonium bromide in $CDCl_3$ at ambient temperature slowly converts it to olefin **12**. This is reminiscent of the thermal lability of the phosphonium chloride **15**, suggesting that bromide ion, like chloride ion, is sufficiently basic to remove a proton from **17** to form **12**.

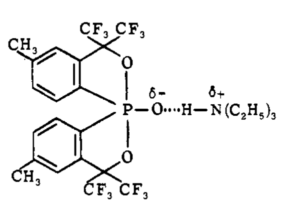
No reaction is detected between hydroxyphosphorane **6** and diazomethane in THF-ether. Addition of $BF_3 \cdot Et_2O$ forms a crystalline 1:1 adduct of **6** and BF_3. Methoxyphosphorane **20** can, however, be prepared from sodium phosphoranoxide **4** and methyl iodide. Phosphorane **20** is rapidly hydrolyzed to give hydroxyphosphorane **6**.

Acidity. The acidities of hydroxyphosphoranes have been important parameters in considering their involvement as intermediates or transition states in nucleophilic substitution at tetracoordinate phosphorus.[2,19] Estimates for the acidities of tetraoxyhydroxyphosphoranes have ranged from pK_a = 9.5-10.0[7c,19] to "strong acids"[9b] which are completely deprotonated by amines[9] or even by as weak a base as dimethylformamide.[9b] The successful synthesis of pure metal phosphoranoxides in this work has made possible the direct determination of the acidities of the corresponding hydroxyphosphoranes in organic solvents. We have observed the degree of protonation of phosphoranoxides with a series of organic acids using NMR techniques.

The acidity of **10** could be expected a priori to be greater than that of **6** by virtue of the highly electronegative fluoroalkoxy ligands attached to phosphorus. In a comparison of **10** and **6** this difference is surely much more important than the small effect of the methyl substituents para to phosphorus in **10**. While **6** is converted by aqueous NaOH to a P^{IV} compound, presumably **21**, **10** is only deprotonated, allowing isolation of crystalline sodium phosphoranoxide **11** as a tetrahydrate. Sodium phosphinate **21** is converted back to **6** upon acidification with hydrochloric acid. Hydroxyphosphorane **10**, but not **6**, is completely deprotonated by potassium bicarbonate in aqueous ethanol, producing the corresponding potassium phosphoranoxide. This salt is practically insoluble in and inert toward water and is easily isolated and purified. The interaction of **10** with triethylamine leads to a crystalline 1:1 complex **22**. This is apparent from the ^1H NMR spectrum of **22** as compared with that of the potassium phosphoranoxide analogue of **11**, both in chloroform solution. The well-defined chemical shifts of the protons ortho to P in the ^1H NMR spectra of hydroxyphosphorane **10**, amine complex **22**, and potassium phosphoranoxide **11** are observed at δ 8.13, 8.30, and 7.95, respectively. In the potassium phosphoranoxide, the δ value of the protons ortho to P is shifted 0.18 ppm to higher field from the position in **10**. This is not the case for **22**. In fact, the corresponding protons of **22** are found not upfield but 0.17 ppm downfield of the position observed for **10**. The change in chemical shift for the CH_2 protons from δ 2.54 for Et_3N to δ 3.15 in the hydrochloride is typical for the reaction with strong acids. The smaller chemical shift change to δ 2.77 for **22** (and to δ 2.70 for an earlier reported[9b] tetraoxyhydroxyphosphorane) is more compatible with the pictured complex than with a dissociated triethylammonium salt. This conclusion is further supported by the observation that treatment of **22** with excess methyl iodide gives a 1:1 mixture of **10** and methyltriethylammonium iodide, rather than the methoxyphosphorane derivative of **10**.



21, $\delta_{^{31}P}$ 34.0 (D_2O)



22, $\delta_{^{31}P}$ -17.6

The potassium analogue of **11** in THF ($\delta_{^{31}P}$ −15.9) is ca. 80% protonated by an equimolar amount of benzoic acid (pK_a = 4.2), as evidenced by the observed $\delta_{^{31}P}$ −17.4 (compare $\delta_{^{31}P}$ −17.8 for **10** and −14.8 for **11**). This estimate of the acidity of **10** was confirmed by titrations using a glass electrode in 80% (v/v) aqueous ethanol. The solubility characteristics of **10** precluded the use of aqueous solutions so corrections were made for the electrode response in 80% ethanol by parallel titration of benzoic acid (pK_a = 4.2 in water). This gave a value of 5.3 ± 0.2 for the pK_a of **10**.

While **11** (or **9**) is not protonated by either water or aqueous ammonium chloride, the more basic sodium phosphoranoxide **4** is protonated by water and the resulting **6** and sodium hydroxide further react to give a mixture of the water-insoluble **6**, water-soluble phosphinate **21**, and sodium hydroxide.

The CH_3 chemical shifts for **6** (δ 1.74 and 1.79) are at lower field than those for the anion of **4** (δ 0.96 and 1.16) by an average of 0.70 ppm ($\Delta\delta_{CH_3}$). This large difference is used to estimate the degree of protonation of **4** upon addition of equimolar amounts of various weak acids. A solution of ca. equimolar amounts of dry nitromethane and **4** gives $\Delta\delta_{CH_3}$ = 0.34. The conclusion that **4** is half protonated (and that the acidities of **6** and nitromethane are essentially identical) was confirmed by the ratio of the integral for CH_3NO_2 plus $^-CH_2NO_2$ to that for the *gem*-dimethyl groups of **4** and **6** in the final mixture (5:24 found, 4.5:24 expected). These observations were repeated after twofold dilution of the solution with nearly identical results. The pK_a of **6** is therefore comparable to that of nitromethane,[20] in the range 10-11.

Bonding and Stability. While the solution structures of phosphoranes are not known,[21] molecular geometries close to TBP[5,22] and square pyramidal[23] have been observed in the crystalline state, as well as intermediate structures.[24] Sulfuranes, on the other hand, appear to more closely approximate TBP structures[25] both as solids and in solution. Tetracoordinate selenium compounds (selenuranes) follow[21,26] the pattern found for sulfuranes. The bonding scheme suggested for these and related[16,17] compounds has been called hypervalent bonding.[27] In this bonding scheme the apical atoms in a TBP structure are bonded to the central atom, e.g., phosphorus, by a three-centered four-electron delocalized bond. This bond is composed of one unoccupied and two occupied molecular orbitals which are constructed from a single p orbital of each atom involved in the linear hypervalent bond. This description implies a weaker and longer bond from the electronegative apical atoms to the partially positively charged central atom (phosphorus in phosphoranes). Electropositive equatorial ligands or electronegative apical ligands are therefore expected to lead to stronger hypervalent bonds.

The relative stability of the two hydroxyphosphoranes **6** and **10** is strongly supportive of this prediction. Both **6** and **10** are expected to be stabilized by the five-membered-ring effect,[2,11] the Thorpe-Ingold effect,[28] and their conformity with electronegativity rules.[2,29] However, it is evident that phosphorane **10** is more stable than **6**. The enhanced electronegativity of the apical oxygens in the fluoroalkoxy ligands increases the electronegativity difference between the central phosphorus and the apical oxygens. This feature contributes to the stability of **10**, as compared with **6**.[27,30]

Experimental Section

Infrared spectra were recorded for $CHCl_3$ solutions. ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts are reported in parts per million downfield from Me_4Si and 85% H_3PO_4, respectively. ^{19}F NMR chemical shifts are reported on the ϕ scale in parts per million upfield from $CFCl_3$. Unless otherwise stated, NMR spectra were obtained for $CDCl_3$ solutions. Electron impact mass spectra were obtained at 70 eV and 150–200 °C source temperature, using the direct insertion probe. Unless otherwise noted, elemental analyses of new compounds were within 0.4% of calculated values. Solutions of products in organic solvents were dried ($MgSO_4$) and the solvent was removed under reduced pressure.

1-Hydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] (6). To 1-methyl-1-(2-bromophenyl)ethanol[31] (21.6 g) and dry THF (150 mL) methylmagnesium bromide (32.2 mL, 3.1 M in ether) was added dropwise with magnetic stirring. Magnesium turnings (2.4 g) were then added, the mixture was refluxed until most of the magnesium dissolved (1.5 h), and $POCl_3$ (7 g) in dry THF (10 mL) was added dropwise at 10 °C. This mixture was boiled for 45 min, cooled, and hydrolyzed with aqueous NH_4Cl. Two extractions with $CHCl_3$ (150 and 100 mL) gave the crude product which was washed with pentane (100 mL) and recrystallized (5.5 g, 40%), mp 181 °C (EtOH): IR 3370 cm^{-1} (OH), 1440 (P–Ph), 1200 (P=O), 960 (P–OC); ^{1}H NMR δ 1.74 (6 H, s, Me), 1.79 (6 H, s, Me), 5.90 (1 H, br s, HO), 7.17–7.60 (6 H, m, HAr), 7.94–8.18 (2 H, m, H ortho to P); ^{1}H NMR (C_5D_5N) δ 1.67 (6 H, s, Me), 1.70 (6 H, s, Me), 7.13 (1 H, s, HO), 7.20–7.57 (6 H, m, HAr), 8.37–8.60 (2 H, m, H ortho to P); ^{31}P NMR (C_5H_5N) δ −12.4 (br); MS *m/e* 301 (M − Me, 68%), 299 (M − OH, 2), 298 (M − H_2O, 7), 283 (M − Me − H_2O, 31), 265 (11), 91 (14), 77 (13), 58 (100). Anal. ($C_{18}H_{21}O_3P$) C, H, P.

1-Hydroxy-1-oxo-3,3′-dimethyl-3*H*-2,1-benzoxaphosphole (13). The aqueous layer from the above preparation of **6** was acidified with 36% HCl and cooled with an ice bath. The crystalline acid **13** was filtered off (0.5 g, 6%), mp 221 °C (EtOH): ^{1}H NMR δ 1.70 (6 H, s, Me), 7.20–7.90 (4 H, m, HAr), 9.80 (1 H, br s, HO); ^{31}P NMR δ 39.3; MS *m/e* 198 (M$^+$, 3%), 183 (M − Me, 100%), 165 (M − Me − H_2O, 24%). Anal. ($C_9H_{11}O_3P$) C, H, P.

Reaction of 6 with $BF_3 \cdot Et_2O$. Hydroxyphosphorane **6** (50 mg) was dissolved in dry THF (5 mL), then $BF_3 \cdot Et_2O$ in ether (0.3 mL) was added. Evaporation of the resulting solution and washing with dry ether gave the product, mp 160 °C (55 mg, 91%): ^{1}H NMR δ 1.93 (6 H, s, Me), 1.97 (6 H, s, Me), 7.70–8.13 (8 H, m, HAr); ^{31}P NMR δ 82.4. Anal. ($C_{18}H_{21}BF_3O_3P$) C, H.

Reaction of 6 with Sodium Hydroxide-*d*. Addition of **6** (60 mg) to NaOD in D_2O (0.5 mL of 0.1 M) formed a suspension which was shaken and then filtered to remove unreacted **6** to give a clear solution, presumably of the salt **21**: ^{1}H NMR (D_2O) δ 1.73 (12 H, s, Me), 7.05–7.62 (8 H, m, HAr); ^{31}P NMR (D_2O) δ 34.0. Acidification (2 N HCl) of the D_2O solution precipitated **6**, identical with an authentic sample (melting point, ^{1}H NMR).

3,3,3′,3′-Tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphospholium] Chloride (15) and 3,3-Dimethyl-1-[2-(1-methyleneethyl)phenyl][3*H*-2,1-benzoxaphosphole] 1-Oxide (12). Hydroxyphosphorane **6** (40 mg) was dissolved in $CDCl_3$ (0.5 mL) and then thionyl chloride (100 mg) was added: ^{1}H NMR δ 1.96 (6 H, s, Me), 1.99 (6 H, s, Me), 7.70–8.10 (8 H, m, HAr); ^{31}P NMR δ 81.8.

This product was not isolated. Upon evaporation of the above solution and brief heating of the residue, a mixture of **12** and **15** (^{1}H NMR) was obtained. Further heating at 60 °C (0.2 mmHg) followed by recrystallization (aqueous EtOH) gave **12** (25 mg, 66%), mp 125–126 °C: ^{1}H NMR δ 1.63 (3 H, s, Me), 1.78 (3 H, s, Me), 2.21 (3 H, m, MeC=C), 5.05 (1 H, m, CH=C), 5.27 (1 H, m, CH=C), 7.17–7.90 (8 H, m, HAr); ^{31}P NMR δ 44.2; MS *m/e* 298 (M$^+$, 100%), 297 (M − H, 23%), 283 (M − Me, 49%), 279 (M − H − H_2O, 11%), 265 (M − Me − H_2O, 22%), 247 (M − Me − $2H_2O$, 28%), 243 (59%), 115 (36%), 91 (24%). Anal. ($C_{18}H_{19}O_2P$) C, H, P.

3,3-Dimethyl-1-[2-(1-methyleneethyl)phenyl][3*H*-2,1-benzoxaphosphole] (12). *n*-Butyllithium (45 mL, 2.3 M in hexane) was added dropwise at −20 °C with stirring to a dry ether (100 mL) solution of 1-methyl-1-(2-bromophenyl)ethanol (10.8 g). The temperature was raised to 32 °C over 50 min. Dropwise addition of $POCl_3$ (3.8 g) at 0 °C gave a mixture which was stirred at ambient temperature for 36 h and then hydrolyzed with ice–water (20 mL). The organic layer yielded the crude product. (The aqueous layer yielded acid **13** (0.65 g) upon acidification.) Column chromatography of the crude product on silica, eluting with 1:1 benzene–ethyl acetate, gave **12** (1.8 g, 24%), identical with a sample prepared from **6** and $SOCl_2$ (vide supra), mp and mmp 125–126 °C, R_f 0.22 (silica, benzene–ethyl acetate, 1:1).

3,3,3′,3′-Tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphospholium] Trifluoromethanesulfonate (17). Trifluoromethanesulfonic acid (3.6 g) was added dropwise to a solution of either **6** or **12** (3.6 g) in chloroform (50 mL). After 1 h at room temperature the solvent was removed under reduced pressure and dry ether (100 mL) was added. Crystallization was induced by a spatula. Filtration and washing with dry ether gave **17** (4.5 g, 88%), mp 153 °C. Recrystallization from THF–ether did not change the melting point: ^{1}H NMR δ 1.97 (6 H, s, Me), 2.01 (6 H, s, Me), 7.63–8.08 (8 H, m, HAr); ^{31}P NMR δ 82.6. Anal. ($C_{19}H_{20}F_3O_5PS$) C, H, P.

1-Phenyl-3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] (18). Phosphonium salt **17** (80 mg), dry THF (10 mL), and phenylmagnesium bromide (1 mL, 3 M in ether) were stirred at ambient temperature for 1 h. The resulting mixture was quenched with aqueous ammonium chloride solution (2 mL, 4 M). The organic layer and $CHCl_3$ (10 mL) extraction gave phosphorane **18** (50 mg, 75%), mp and mmp 195 °C. The ^{1}H, ^{31}P, and ^{13}C NMR spectra obtained for this sample were identical with those of an authentic sample.[16]

1,3,3,3′,3′-Pentamethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] 19. Phosphonium salt **17** (60 mg), dry THF (5 mL), and methylmagnesium bromide (0.4 mL of 3.1 M in ether) were stirred for 10 min at ambient temperature and allowed to stand for 3 h. Quenching with 2 mL of aqueous NH_4Cl (4 M) (2 mL of 4 N), followed by $CHCl_3$ (10 mL) extraction, gave the crude **19**, which was not purified further: ^{1}H NMR δ 1.55 (12 H, s, Me), 1.95 (3 H, d, $^2J_{HP}$ = 16 Hz, MeP), 7.12–7.50 (6 H, m, HAr), 8.12–8.24 (2 H, m, H ortho to P); ^{31}P NMR δ −39.2.

Sodium 3,3,3′,3′-Tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] 1-Oxide (4). Sodium hydride (0.73 g of a commercial 57% oil dispersion) was placed in a conical 250-mL flask and washed twice with dry pentane (100 mL). Dry THF (50 mL) was then added, followed by **6** (4.0 g). Molecular hydrogen was evolved rapidly, through a $CaCl_2$ tube attached to the flask. Filtration and evaporation of the THF gave the desired salt which was washed with dry pentane and dried in the oven at 115–120 °C, giving 3.4 g (79%), mp > 280 °C: ^{1}H NMR δ 0.96 (6 H, s, Me), 1.16 (6 H, s, Me), 6.98–7.27 (6 H, m, HAr), 7.90–8.12 (2 H, m, H ortho to P); ^{1}H NMR (THF-d_8) 1.33 (6 H, s, Me), 1.45 (6 H, s, Me), 6.90–7.31 (6 H, m, HAr), 8.20–8.41 (2 H, m, H ortho to P); ^{31}P NMR (THF) δ −26.9. Anal. ($C_{18}H_{20}O_3PNa$) C, H, P.

1-Methoxy-3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] (20). The sodium derivative of **4** (0.2 g) in dry THF (5 mL) was treated with methyl iodide (0.2 g) in the dark at ambient temperature for 5 days. The solvent was evaporated and the residue was extracted with dry pentane to give **20** (150 mg, 77%), mp 115 °C: ^{1}H NMR δ 1.73 (12 H, s, Me), 3.46 (3 H, d, $^3J_{HP}$ = 15 Hz, MeP), 7.12–7.55 (6 H, m, HAr), 8.13–8.34 (2 H, m, H ortho to P); ^{31}P NMR (THF) δ −25.6. Anal. ($C_{19}H_{23}O_3P$) C, H, P.

Reaction of 4 with Nitromethane. Sodium salt **4** (49 mg) was dissolved in 0.4 mL of purified (basic Al_2O_3) $CHCl_3$ (0.4 mL) containing 1% Me_4Si: ^{1}H NMR δ 0.96 (6 H, s, Me), 1.16 (6 H, s, Me). Dry nitromethane (9.6 mg) was added and ^{1}H NMR was recorded after 2 h: δ 1.40 (12 h, br s, Me), 4.22 (2.5 H, s, CH_3NO_3 and $^-CH_2NO_2$). $\Delta\delta = 0.34$ ppm (calcd 0.35 ppm for 50% protonation of **4** by nitromethane).

Protonation and Hydrolysis of 4. Treatment of **4** with dilute HCl quantitatively converted it to **6**. Addition of excess water to this salt gave a ca. 1:1 mixture of the water-insoluble **6** and the water-soluble sodium phosphinate **21** (^{31}P NMR (D_2O) δ 34.0), along with sodium hydroxide. Acidification of the aqueous layer yielded the hydroxyphosphorane **6**.

1-(2-Bromo-5-methylphenyl)-1-trifluoromethyl-2,2,2-trifluoroethanol (8).[32] A solution of 1-(2-amino-5-methylphenyl)-1-trifluoromethyl-2,2,2-trifluoroethanol[33] in 48% HBr (300 mL) was cooled to 0 °C and sodium nitrite (21 g) in water (50 mL) was added dropwise with stirring. The resulting solution was slowly (1.5 h) added to a suspension of cuprous bromide (57.4 g) in 48% HBr (100 mL) at 0 °C and with vigorous stirring. This mixture was then heated for 30 min on a steam bath, followed by steam distillation, which was stopped after 42 g of the crude product was collected. Recrystallization from pentane yielded the desired product (36 g, 36%), mp 46 °C: ^{1}H NMR δ 2.33 (3 H, s, Me), 5.30 (1 H, br s, HO), 7.01–7.57 (3 H, m, HAr); ^{19}F NMR ϕ 74.17 (s, CF_3); MS *m/e* 336 (M^+, 43%), 267 (M − CF_3, 65%), 223 (72%), 197 (76%), 153 (100%), 91 (93%), 69 (CF_3, 48%). Anal. ($C_{10}H_7BrF_6O$) C, H, Br.

1-Hydroxy-3,3,3′,3′-tetrakis(trifluoromethyl)-5,5′-dimethyl-1,1′-spiro[3*H*-2,1-benzoxaphosphole] (10). Methylmagnesium bromide (8.8 mL of 3.1 M in ether) was added to a dry THF (50 mL) solution of **8** (9.1 g), followed by magnesium turnings (0.66 g). This mixture was refluxed for 3 h. Phosphorus oxychloride (1.8 g) in dry THF (5 mL) was added dropwise to the cooled dark-brown solution and it was boiled for 45 min. Quenching with aqueous NH_4Cl solution (50 mL) followed by $CHCl_3$ extraction yielded the crude product, from which 1-(5-methylphenyl)-1-trifluoromethyl-2,2,2-trifluoroethanol (0.8 g) was removed under reduced pressure. The residue was washed with pentane to give the crystalline magnesium phosphoranoxide **9** (4.1 g, 65%), mp >360 °C: ^{1}H NMR δ 2.48 (6 H, s, Me), 7.24–7.52 (4 H, m, HAr), 8.06–8.30 (2 H, m, H ortho to P); ^{31}P NMR (THF) δ −17.8; ^{19}F NMR ϕ 74.66 (6 F, q, $^4J_{FF}$ = 9 Hz, CF_3), 75.65 (6 F, q, $^4J_{FF}$ = 9 Hz, CF_3). Anal. ($C_{40}H_{24}F_{24}O_6MgP$) C, H, P, Mg.

A solution of **9** (3.5 g) in 96% ethanol (25 mL) was treated with 5 N sodium hydroxide (10 mL). Evaporation of the solvent and washing the residue with water (100 mL) gave, after 16 h at 125 °C (oven), 3.2 g (80%) of the tetrahydrate of **11**, mp >250 °C, ^{31}P NMR (THF) δ −14.8. Anal. ($C_{20}H_{12}F_{12}O_3PNa\cdot 4\ H_2O$) C, H, P.

Stirring a suspension of **11** (3 g) in 1:1 $CHCl_3$–water (80 mL) and concentrated HCl (2 mL) for 5 min gave, after the usual workup, **10** (2.4 g, 92%), mp 168 °C (pentane): ^{1}H NMR δ 2.43 (6 H, s, Me), 3.96 (1 H, br s, HO), 7.25–7.47 (4 H, m, HAr), 8.13 (2 H, dd, $^3J_{HH}$ = 8, $^3J_{HP}$ = 11 Hz, H ortho to P); ^{31}P NMR (THF) δ −17.8; ^{19}F NMR ϕ 74.72 (6 F, q, $^4J_{FF}$ = 9 Hz), 75.61 (6 F, q, $^4J_{FF}$ = 9 Hz, CF_3); MS *m/e* 560 (M^+, 16%), 543 (M − OH, 7%), 541 (M − F, 8%), 491 (M − CF_3, 75%), 422 (M − $2CF_3$, 1%), 321 (11%), 240 (43%), 211 (M − $2CF_3{}^{2+}$, 7%), 151 (10%), 69 (CF_3, 35%), 58 (21%), 43 (100%). Anal. ($C_{20}H_{13}F_{12}O_3P$) C, H, P.

1-Hydroxy-1-oxo-3,3-bis(trifluoromethyl)-5-methyl-3*H*-2,1-benzoxaphosphole (14). The aqueous solution obtained from washing the sodium phosphoranoxide **11** in the above procedure was acidified (36% HCl) and extracted with chloroform, giving the acid **14** (0.3 g), mp 188 °C: ^{1}H NMR δ 2.50 (3 H, s, Me), 7.20–7.90 (3 H, m, HAr), 8.80 (1 H, br s, HO); ^{31}P NMR (THF) δ 31.3; ^{19}F NMR δ 75.75 (s, CF_3); MS *m/e* 320 (M^+, 61%), 251 (M − CF_3, 86%), 203 (25%), 201 (100%), 173 (16%). Anal. ($C_{10}H_7F_6O_3P$) C, H, P.

Potassium 3,3,3′,3′-Tetrakis(trifluoromethyl)-5,5′-dimethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] 1-Oxide (Such as 11). Hydroxyphosphorane **10** (0.2 g) was treated in ethanol (5 mL) with potassium carbonate or bicarbonate (0.1 g) in water (2 mL). Evaporation left a residue which was washed with distilled water. The crystalline salt (0.1 g, 93%) was dried in an oven at 110 °C for 2 h, mp >250 °C: ^{1}H NMR δ 2.40 (6 H, s, Me), 7.04–7.50 (4 H, m, HAr), 7.95 (2 H, dd, $^3J_{HH}$ = 9, $^3J_{HP}$ = 11 Hz, H ortho to P); ^{31}P NMR (THF) δ −15.9. Anal. ($C_{20}H_{12}F_{12}O_3P$) C, H, P.

1-Hydroxy-3,3,3′,3′-tetrakis(trifluoromethyl)-5,5′-dimethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole]–Triethylamine Complex (22). Hydroxyphosphorane **10** (53 mg) and excess triethylamine were dissolved in chloroform (3 mL). Evaporation of the solvent left a crystalline compound (51 mg, 82%), mp 161–163 °C (pentane): ^{1}H NMR δ 1.00 (9 H, t, $^3J_{HH}$ = 7 Hz, *Me*CH_2), 2.40 (6 H, s, Me), 2.77 (6 H, q, $^3J_{HH}$ = 7 Hz, *CH_2*Me), 7.18–7.37 (4 H, m, HAr), 8.19–8.40 (2 H, m, H ortho to P); ^{31}P NMR δ −17.6.

Treatment of this complex with excess MeI gives 1:1 mixture of hydroxyphosphorane **10** and methyltriethylammonium iodide: ^{1}H NMR δ 1.40 (9 H, t, $^3J_{HH}$ = 7 Hz, Me), 2.51 (6 H, s, MeAr), 3.19 (3 H, s, MeN), 3.55 (6 H, q, $^3J_{HH}$ = 7 Hz, CH_2), 3.63 (1 H, s, HO), 7.30–7.50 (4 H, m, HAr), 8.13 (2 H, dd, $^3J_{HH}$ = 8, $^3J_{HP}$ = 11 Hz, H ortho to P).

Titrimetric pK_a Measurement for 10. Solutions of **10** or benzoic acid (ca. 0.025 M) in 80% (v/v) aqueous ethanol were titrated with 0.2 M NaOH in the same solvent. The measured pK_a for **10** was greater than that for benzoic acid by 1.1 ± 0.2 log units. Since the pK_a of benzoic acid is 4.2[34] in water, we take pK_a for **10** in water to be 5.3 ± 0.2.

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