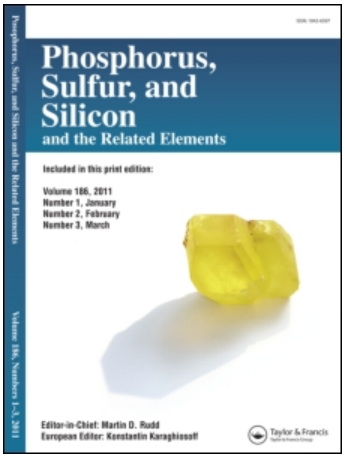

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INHIBITION OF PSEUDOROTATION IN SOME MONOCYCLIC PENTAOXYPHOSPHORANES

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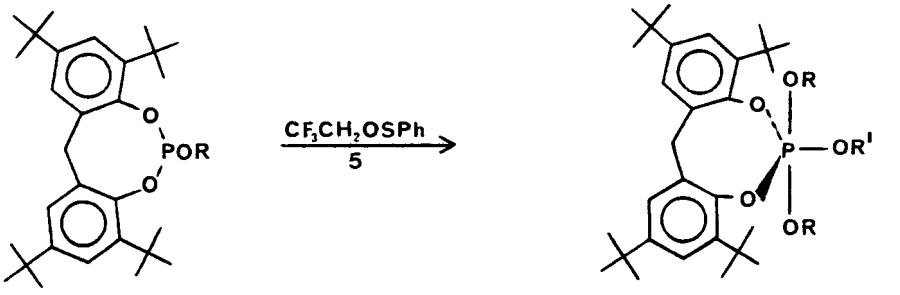
Phosphoranes were prepared by allowing 2,4,8,10-tetra-tert-butyl-6-(2,2,2,trifluoroethoxy)-12H-dibenzo[d,g][1,3,2]dioxaphosphocin, the analogous ethoxy compound, 2,4,8,10-tetra-tert-butyl-6-(2,2,2,-trifluoroethoxy)-dibenzo[d,f][1,3,2]dioxaphosphepin and the analogous compound without tert-butyl groups to react with trifluoroethyl benzenesulfenate. The first three phosphoranes showed significant barriers to intramolecular ligand reorganization, 14–16 kcal/mole. The phosphorane without the tert-butyl groups had a barrier too low to measure. These observations are discussed in terms of steric inhibition of pseudorotation.

The chemistry of pentaoxyphosphoranes has been extensively studied for the past two decades.[1] One of the most interesting aspects of the chemistry of these materials is their ability to undergo facile intramolecular permutational isomerization, pseudorotation. Although variable temperature NMR investigations have been conducted on many pentaoxyphosphoranes, it appears that in only a few cases has pseudorotation been slowed sufficiently so that its cessation has been observed by NMR.[2] The substances in question are caged bicyclic phosphoranes with special structural features which constrain the pseudorotation process at relatively high temperatures. Simple acyclic and monocyclic pentaoxyphosphoranes which have been investigated in the past have not had NMR temperature dependent spectra.



1 R = CH_2CF_3

2 R = CH_2CH_3

3 R = R' = CH_2CF_3

4 R = CH_2CF_3; R' = CH_2CH_3

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Recently trivalent phosphorus compounds derived from 2.2′-alkylidine bisphenols have become available.[3] Compounds, **1** and **2**, have been prepared in this study and they have been converted into the pentaalkoxyphosphoranes, **3** and **4**, by allowing them to react with the trifluoroethoxy benzenenesulfenate, **5**.[4] The ^{31}P NMR spectrum of **3** has a resonance at δ −78.5 which is that expected for the proposed structure.[4] The other NMR spectral data and analysis are in complete agreement with the suggested structure. The tables contain the NMR data.

The ^{1}H NMR spectrum of **3** at 100°C has a doublet at δ 3.78, $^{5}J_{POCCCH_2} = 2.7$ Hz for the hydrogens of the methylene group which bridges the two benzene rings. Similarly the methylene hydrogens of the trifluoroethoxy groups are found as doublets of quartets at δ 4.15, $^{3}J_{HCOP} = 4.2$ Hz and $^{3}J_{HCCF} = 8.0$ Hz. A static trigonal bipyramidal (TBP) or square pyramidal (SP) structure for **3** would not lead to such a simple ^{1}H NMR spectrum. The ^{19}F NMR spectrum is a triplet at δ −75.30, $^{3}J_{HCCF} = 8.0$ Hz. Such a spectrum would not be found for a static molecule. Clearly the molecule is fluxional at 100°C and the motion must be intramolecular. If ionization was occurring then the ^{1}H couplings to phosphorus would be lost. On cooling the ^{19}F NMR spectrum showed three different resonances for nonequivalent trifluoromethyl groups. Such a spectrum can arise if **3** is no longer undergoing intramolecular permutational isomerization. The structure of **3** with the ring spanning diequatorial positions with two trifluoroethoxy groups in apical positions and the remaining one in an equatorial position leads to nonequivalent trifluoroethoxy groups provided that the bridging methylene group is no longer fluxional. That this is the case is demonstrated by the ^{1}H NMR spectrum which at −27°C shows the two hydrogens at δ 3.52, $^{2}J_{HCH} = 13.6$ Hz and $^{5}J_{POCCCH} = 1.9$ Hz and δ 4.11, $^{2}J_{HCH} = 13.6$ Hz and $^{5}J_{POCCCH} = 2.8$ Hz. Clearly the equivalency of these two hydrogens which was found at 100°C has disappeared at −27°C which indicates that the motion that led to their equivalency is no longer occurring.

Further evidence for the inhibition of pseudorotation is provided by the ^{1}H NMR spectrum which shows that the three groups of methylene hydrogens on carbon bonded to oxygen are nonequivalent. Two of these groups have virtually identical chemical shifts, $\delta = 4.50$ while the remaining is significantly shielded and it is found at δ 3.13. An inspection of a model shows that when the ring is di-e,e, the trifluoroethoxy group *trans* to the bridging methylene group can be in a shielding region formed by the "tent-like" arrangement of the benzene rings. This conformation may be favored because of repulsions between the trifluoromethyl group of this apical substituent and the equatorial trifluoroethoxy group.[5]

Alternatively one might consider a TBP structure in which the ring spans e–a positions. Such a structure would have nonequivalent benzene rings and t-butyl groups. Neither the ^{1}H or ^{13}C NMR spectra indicate that this is the case. Similar arguments can be used to eliminate various SP structures which incidentally are not expected for simple monocyclic pentaoxyphosphoranes.[1a]

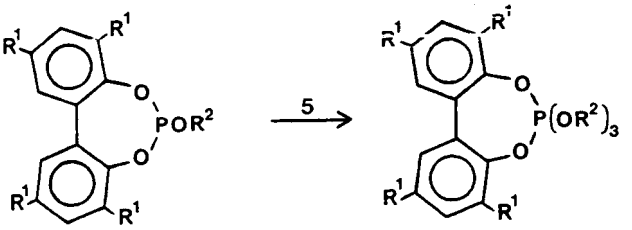
The activation energy, computed from the variable temperature ^{19}F NMR spectra, for the process that renders the trifluoromethyl groups equivalent is 15.4 kcal/mol.

Compound **4** only differs structurally from **3** in that one trifluoroethoxy group is replaced by an ethoxy group. The ^{31}P NMR spectrum has a single resonance at δ −79 which is that expected of a pentaoxyphosphorane. The variable temperature ^{19}F NMR spectra of **4** show that below 52°C there are two nonequivalent trifluoro-

methyl groups at δ −75.33 and −76.43. The activation energy required to render them equivalent is 15.7 kcal/mole which is essentially identical to that found for **3**.

Both the ^1H and the ^{13}C NMR spectra require that the eight membered ring span diequatorial positions. The low temperature ^1H NMR spectrum of the OCH_2 region is quite interesting. There are two absorptions at δ 3.27 and δ 4.62 for OCH_2CF_3 groups. Once again one group is shielded as was found in **3**. The $^3J_{HCOP}$ values of 2.9 Hz and 4.5 Hz for these hydrogens indicate apical placements whereas $^3J_{HCOP}$ = 7.1 Hz for the methylene hydrogens of the ethoxy group is that expected for an equatorial group.[4,6]

In order to investigate the structural effects of the bridging methylene group and the t-butyl groups on rates of pseudorotation and thermodynamically favored structure, compounds **6** and **7** were prepared and converted into the phosphoranes, **8** and **9**.



6 $R^1 = C(CH_3)_3$; $R^2 = CH_2CF_3$ **8** $R^1 = C(CH_3)_3$; $R^2 = CH_2CF_3$

7 $R^1 = H$; $R^2 = CH_2CF_3$ **9** $R^1 = H$; $R^2 = CH_2CF_3$

Compound **8** has δ −67.8 in its ^{31}P NMR spectrum which clearly indicates a phosphorane structure. The variable temperature ^{19}F NMR spectrum showed below 15°C, the coalescence temperature, fluorine resonances for two different trifluoromethyl groups. The activation energy required to render the trifluoromethyl groups equivalent is 14.6 kcal/mole. The ^1H and ^{13}C NMR spectra show that there are two sets of t-butyl groups. A structure for **8** is uniquely defined by these data. The seven membered ring spans two equatorial positions with two apical trifluoroethoxy groups. This is of course the structure predicted on the basis of strain and electronegatively considerations i.e. no strain is introduced in the ring and the more electronegative trifluoroethoxy groups prefer apical positions.

Compound **9** had a ^{31}P NMR absorption δ −63.1 which is of course within the range expected for a pentaoxyphosphorane. The variable temperature ^{19}F NMR spectra showed no change down to −55°C. This result can be due to no inhibition of intramolecular ligand reorganization or accidental equivalency of the NMR absorptions over the temperature range investigated. This latter explanation does not seem too plausible in view of the fact that differences were found in all the other cases.

In all of the structures investigated pseudorotation is limited to ee → ea rearrangements of the eight and seven membered rings. It seems reasonable that in the ea conformation the t-butyl groups ortho to the bonding phenolic oxygens interact

TABLE I[a]

Compound	T °C	31p	19_F	1_H					
1	24[b]	125.9	−75.1 (d of t) J_{FCCH} = 8.6 J_{FCCOP} = 0.6		1.35 (s)	1.51 (s)	3.41 (d) J_{HCH} = 12.4	4.46 (d of d) J_{HCH} = 12.4 J_{HP} = 2.9	4.65 (d of q) J_{HCCF} = 8.8 J_{HCOP} = 5.5	
					18 H $C(CH_3)_3$	18 H $C(CH_3)_3$	1 H H—C—H	1 H H—C—H	2 H —O—CH_2—	
2	24[c]	128.6		f	1.45 (s)	1.58 (s)	3.58 (d) J_{HCH} = 12.8	4.56 (d of d) J_{HCH} = 12.8 J_{HP} = 2.8	4.64(d of q) J_{HCCH} = 6.8 J_{HCOP} = 6.8	
				3 H CH_3	18 H $C(CH_3)_3$	18 H $C(CH_3)_3$	1 H H—C—H	1 H H—C—H	2 H —O—CH_2—	
3	−27[b]				1.23 (s)	1.34 (s)	3.52 (d) J_{HCH} = 13.6 J_{HP} = 1.9	4.11 (d of d) J_{HCH} = 13.6 J_{HP} = 2.8	3.13 (d of q) J_{HCCF} = 8.4 J_{HCOP} = 3.0	4.50 (d of q) J_{HCCF} = 8.2 J_{HCOP} = 3.8
					18 H $C(CH_3)_3$	18 H $C(CH_3)_3$	1 H H—C—H	1 H H—C—H	2 H O—CH_2—	4 H —O—CH_2—
	−19[b]		−73.6 (t) J_{FCCH} = 8.0 −73.7 (t) J_{FCCH} = 8.0 −74.9 (t) J_{FCCH} = 8.0							
	24[b] 100[d]	−78.5	−75.0 (t) J_{FCCH} = 8.0		1.33 (s)	1.45 (s)	3.78 (d) J_{HP} = 2.7	4.18 (d of q) J_{HCOP} = 4.2 J_{HCCF} = 8.8		
					18 H $C(CH_3)_3$	18 H $C(CH_3)_3$	2 H H—C—H	6 H —O—CH_2		
4	−7[b]			f	1.37 (s)	1.50 (s)	3.61 (d) J_{HCH} = 14.0	4.25[g]		
				3H CH_3	18 H $C(CH_3)_3$	18 H $C(CH_3)_3$	1 H H—C—H			
	24[b] 99[d]	−79.0	−75.3 (t) J_{FCCH} = 8.5	f	1.36 (s)	1.50 (s)	3.86 broad	4.11 broad		
				3 H CH_3	18 H $C(CH_3)_3$	18 H $C(CH)_3$	2 H H—C—H	6 H O—CH_2—		

6	24[e]	131.6	−75.1 (d of t) J_{FCCH} = 8.5 J_{FCCOP} = 1.2	1.26 (s) 18 H $C(C\underline{H}_3)_3$	1.51 (s) 18 H $C(C\underline{H}_3)_3$	3.96 (d of q) J_{HCCF} = 8.4 J_{HCOP} = 6.5 2 H $O—C\underline{H}_2—$
7	24[e]	134.7	−75.2 (d of t) J_{FCCH} = 8.0 J_{HCOP} = 1.7			4.07 (d of q) J_{HCCF} = 8.0 J_{HCOP} = 8.0 2 H $O—C\underline{H}_2—$
8	35[b]	−67.6	−75.2 (t) J_{FCCH} = 8.3	1.50 (s) 18 H $C(C\underline{H}_3)_3$	1.63 (s) 18 H $C(C\underline{H}_3)_3$	4.54 (d of q) J_{HCCF} = 8.4 J_{HCOP} = 4.8 6 H $O—C\underline{H}_2—$
9	24[c]	−63.1	−75.5 (t) J_{FCCH} = 8.4			4.20 (d of q) J_{HCCF} = 8.4 J_{HCOP} = 8.0 6 H $O—C\underline{H}_2—$
	−55[c]		−75.3 (t) broad J_{FCCH} = 7.5			

[a] See experimental for details of NMR experiment. In the ^1H NMR spectra of these compounds all have absorptions in the aromatic region. In most cases the integrated area is correct, in others the integrated area for the aromatic region is high. This is owing to the presence of diphenyl disulfide.

[b] The solvent is CD_2Cl_2.

[c] The solvent is $CDCl_3$.

[d] The solvent is CD_3–C_6D_5.

[e] The solvent is C_6D_6.

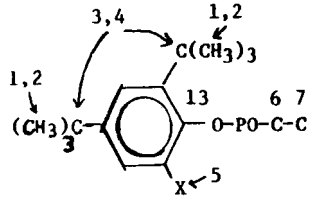
[f] The hydrogens of the CH_3 group are partially obscured by those of the t-butyl groups.

TABLE II

^{13}C NMR Spectral Data[a]

Cpd/C#[b]	1	2	3	4	5	6	7	8	9	10	11	12	13
1[c]	31.1 (d) J = 4.1	31.6	34.9	35.4	35.4	59.9 (d of q) J = 36.7 J = 6.1	124.2 (d of q) J = 277.2 J = 4.3	123.7	125.5 (d) J = 0.7	136.3 (d) J = 3.8	142.0 (d) J = 3.7	145.3 (d) J = 7.8	147.9 (d) J = 1.3
2[d]	31.4 (d) J = 4.1	32.0	35.0	35.7 (d) J = 7.4	35.9	59.9 (d) J = 4.4	17.3 (d) J = 3.7	123.4	125.4	136.4 (d) J = 3.9	141.8 (d) J = 3.7	146.4 (d) J = 7.7	146.9 (d) J = 1.2
3[c]	30.8	31.5	34.7	35.2	34.3 (d) J = 1.3	64.2 f	9 = g	128.2 (d) J = 1.6	125.8 (d) J = 2.4	134.0 (d) J = 3.8	138.2 (d) J = 6.9	147.3 (d) J = 2.5	148.7 (d) J = 13.4
4[c]	30.9	31.6	34.6	34.7	35.3 (d) J = 0.5	65.0 f	15.8 (d) J = 9.6	122.5 (d) J = 1.3	126.0 (d) J = 2.2	133.4 (d) J = 3.6	128.1 (d) J = 6.8	146.7 (d) J = 2.4	148.3 (d) J = 13.2
6[d]	31.2 (d) J = 2.7	31.8	35.0	35.7		60.8 (q) J = 36.7	123.6 (d of q) J = 277.8 J = 4.3	125.1	127.0	132.9 (d) J = 3.5	140.6 (d) J = 1.7	145.9 (d) J = 5.8	147.8
7[d]						60.4 (d of q) J = 36.7 J = 2.1	123.2 (d of q) J = 275.4 J = 4.3	121.9	125.7	129.7	130.3 (d) J = 0.7	131.0 (d) J = 3.3	146.6 (d) J = 5.5
8[c]	30.8	31.5	34.8	35.6		65.7[f]	9 = g	124.7	126.3 (d) J = 1.3	130.3 (d) J = 1.4	139.7 (d) J = 8.7	146.7 (d) J = 1.8	148.6 (d) J = 13.5
9[e]						67.6 (d of q) J = 29.0 J = 9.4	122.5 (d of q) J = 278.9 J = 4.8	113.2 (d) J = 4.8	115.4 (d) J = 1.8	117.8 (d) J = 14.1	118.6	135.7 (d) J = 10.7	141.0

[a] See experimental for details of NMR experiments. Since all spectra are proton decoupled the coupling constants listed reflect coupling to fluorine and phosphorus.
[b] The numbering system is as follows:



8 and 9 aromatic carbons with hydrogens. 10–13 aromatic carbons without hydrogens.
[c] The solvent is CD_2Cl_2.
[d] The solvent is C_6D_6.
[e] The solvent is $CDCl_3$.
[f] The resonance is very broad.
[g] The resonance is obscured.
[h] The C of the CF_3 can not be seen.

sterically more strongly with the other ligands bonded to phosphorus than they do in the ee conformation. Such an interaction has been totally removed in **9** and thus pseudorotation is no longer inhibited. This is of course not the first instance of steric effects on pseudorotation rates.[1] These are interesting examples and they provide the first examples of inhibition of pseudorotation in monocyclic pentaoxyphosphoranes.

EXPERIMENTAL

All solvents were of spectroscopic grade and they were dried prior to use, with appropriate drying agents. All deuterated solvents were obtained commercially at > 99.8% purity. Commercially available starting materials were verified for identity and purity by NMR spectroscopy and/or TLC.

All reactions were carried out in oven or flame-dried apparatus under a nitrogen atmosphere.

^{1}H NMR spectra were obtained on Varian Model T-60 and FT-80 spectrometers. All chemical shifts are reported in ppm relative to internal tetramethylsilane (TMS). All ^{19}F, ^{31}P, ^{13}C NMR spectra were taken on a Varian Model FT-80 spectrometer equipped with a 5 or 10 mm, variable temperature, broad band probe. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{31}P NMR were acquired using a 45° flip angle, one second repetition rate with no pulse delay and with full proton decoupling. ^{13}C NMR chemical shifts are reported in ppm relative to TMS. The ^{13}C NMR spectra were obtained using full proton decoupling a 30° flip angle, and a two second repetition rate with no pulse delay. All ^{19}F chemical shifts are reported in ppm relative to trichlorofluoromethane.

Preparation of 2,4,8,10-Tetra-tert-Butyl-6-(2,2,2,-Trifluoroethoxy)-12H-Dibenzo [d,g][1,3,2]dioxaphosphocin (**1**). To a solution of 27.47 g (0.2 mol) of phosphorus trichloride in 200 ml of toluene at 5°C was added dropwise a solution of 84.94 g (0.2 mol) of 2,2′-methylenebis (4,6-di-*tert*-butylphenol) and 40.48 g (0.4 mol) of triethylamine in 250 ml of toluene. The reaction mixture was stirred at room temperature until the bisphenol had been consumed as determined by TLC. To the reaction mixture at 5°C was added 20.24 g (0.2 mol) of triethylamine and then 20.01 g (0.2 g) of 2,2,2-trifluoroethyl alcohol was added dropwise. The reaction mixture was stirred for 15 hours at room temperature and the triethylamine hydrochloride was removed by filtration. The volatiles were removed *in vacuo* and the residue was recrystallized from an acetonitrile : toluene mixture to give 87.17 g (79%) of a white solid, mp 182–183°C; Anal. Calcd. for $C_{31}H_{44}F_3O_3P$: C, 67.4; H, 8.0, Found: C, 67.5; H, 8.1.

Preparation of 2,4,8,10-Tetra-tert-Butyl-6-Ethoxy-12H-Dibenzo[d,g][1,3,2] dioxaphosphocin (**2**). To a solution of 27.47 g (0.2 mol) of phosphorus trichloride in 200 ml of toluene at 5°C was added dropwise a solution of 84.94 g (0.2 mol) of 2,2′-methylenebis (4,6-di-tert-butylphenol) and 40.48 g (0.4 mol) of triethylamine in 250 ml of toluene. The reaction mixture was stirred at room temperature until all of the starting bisphenol was reacted as determined by TLC. To the reaction mixture at 5°C was added 20.24 g (0.2 mol) of triethylamine and then 9.21 g (0.2 mol) of ethyl alcohol was added dropwise. The reaction mixture was stirred for 15 hours at room temperature. The triethylamine hydrochloride was removed by filtration and the volatiles were removed *in vacuo*. The residue was recrystallized from an acetonitrile : toluene mixture to give 24.23 g (24.3%) of a white solid, mp 228–230°C.

Adduct of 2,4,8,10-Tetra-tert-Butyl-6-(2,2,2-Trifluoro)-12H-Dibenzo [d,g][1,3,2] dioxaphosphocin with Two Moles of 2,2,2-Trifluoroethyl Benzenesulfenate (**3**). To a stirred solution of 0.28 g (0.5 mmol) of 2,4,8,10-tetra-*tert*-butyl-6-(2,2,2-trifluoroethyl)-12H-dibenzo[d,g][1,3,2]dioxaphosphocin in 2 ml of dichloromethane-d_2 at −78°C was added a solution of 0.21 g (1 mmol) of 2,2,2-trifluoroethyl benzenesulfenate in 0.5 ml of the same solvent. The reaction mixture was allowed to warm to room temperature, at which time the ^{31}P NMR spectrum of the reaction mixture had a resonance at δ −78.5. The solvent was removed *in vacuo* and the residue was recrystallized from petroleum ether (bp 35–60°C) to give 0.13 g (35%) of a white solid, mp 190–193°C; Anal. Calcd. for $C_{35}H_{48}F_9O_5P$: C, 56.0; H, 6.4. Found: C, 56.3; H, 6.4.

Adduct of 2,4,8,10-Tetra-tert-Butyl-6-Ethoxy-12H-Dibenzo[d,g][1,3,2]dioxaphosphocin With Two Moles of 2,2,2-Trifluoroethyl Benzenesulfenate (**4**). To a stirred solution of 1.0 g (0.5 mmol) of 2,4,8,10-tetra-tert-butyl-6-ethoxy-12H-dibenzo[d,g][1,3,2] dioxaphosphocin in 2 ml of dichloromethan-d_2 at −78°C was added a solution of 0.42 g (2.0 mmol) of 2,2,2-trifluoroethyl benzenesulfenate in 0.5 ml of the same solvent. The reaction mixture was allowed to warm to room temperature. All spectral data were acquired on this solution.

Preparation of 2,2,2-Trifluoroethyl Benzenesulfenate (**5**). The sulfenate was prepared using the procedure reported by D. B. Denney et al[4] with minor modifications.

To a solution of 11.00 g (0.11 mol) of 2,2,2-trifluoroethyl alcohol and 11.13 g (0.22 mol) of triethylamine in 150 ml of dry diethyl ether at −78°C was added dropwise 14.46 g (0.10 mol) of benzenesulfenyl chloride. The reaction mixture was stirred for one hour at 0°C and the suspension of triethylamine hydrochloride was removed by filtration. The volatiles were removed *in vacuo* and the residue was distilled to give 14.14 g (68%) of a yellow liquid, bp 40–41°C, 0.025 mm (lit.[4] 47°C, 0.05 mm).

Preparation of 2,4,8,10-*Tetra-tert-Butyl*-6-(2,2,2-*Trifluoroethoxy*)-*Dibenzo*[*d,f*][1,3,2]*dioxaphosphepin* (**6**). To a solution of 27.47 g (0.2 mol) of phosphorus trichloride in 200 ml of toluene at 5–10°C was added a solution of 82.13 g (0.2 mol) of 3,3′,5,5′-tetra-*tert*-butyl-biphenyl-2,2′-diol and 40.48 g (0.4 mol) of triethylamine in 250 ml of toluene over a two hour period. The reaction mixture was stirred at room temperature until disappearance of starting biphenyl-2,2′diol was indicated by TLC. The reaction mixture was then cooled to 10°C and a solution of 20.24 g (0.2 mol) of triethylamine in 10 ml of toluene was added followed by 20.01 g (0.2 mol) of 2,2,2-trifluoroethyl alcohol. The reaction mixture was stirred at room temperature for 15 hours and then the suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was purified by recrystallization from acetonitrile followed by flash chromatography to give 38.9 g (37%) of a white solid mp 135–139°C. Anal. Calcd. for $C_{30}H_{42}F_3O_3P$: C, 66.9; H, 7.9. Found: C, 67.2; H, 8.0.

Preparation of 6-Chloro-Dibenzo [*d,f*][*1,3,2*]*dioxaphosphepin*. To 188 g (1.0 mol) of o,o′-biphenol was added, in one portion, 483 g (3.5 mol) of phosphorus trichloride. The reaction mixture was heated to 120–130°C (bath) until no more hydrogen chloride was evolved. Excess phosphorus trichloride was removed by distillation at atmospheric pressure. The residual oil was distilled to yield 228.0 g (91%), bp 192°C, 15 mm (lit.[7] 140°C, 0.2 mm).

Preparation of 6-(*2,2,2-Trifluoroethoxy*)-*Dibenzo*[*d,f*][*1,3,2*]*dioxaphosphepin* (**7**). To a solution of 6.0 g (0.06 mol) of 2,2,2-trifluoroethyl alcohol and 4.7 g of (0.06 mol) pyridine dissolved in 100 ml of ether at 0–5°C was added 15 g (0.06 mol) of 6-chloro-dibenzo [d,f][1,3,2]dioxaphosphepin dissolved in 100 ml of ether. The reaction mixture was stirred for 2 hours at room temperature. The pyridine hydrochloride was removed by filtration. The volatiles were removed *in vacuo* and the residual oil was distilled to yield 15.0 g (85%) of the phosphite, **7**, b.p. 140–143°C, 0.2 mm. Anal. Calcd. for $C_{14}H_{10}F_3O_3P$: C, 53.52; H, 3.19. Found: C, 53.72; H, 3.36.

Adduct of 2,4,8,10-Tetra-tert-Butyl-6-(*2,2,2-Trifluoroethoxy*)-*Dibenzo*[*d,f*][*1,3,2*]*dioxaphosphepin With Two Moles of* 2,2,2-*Trifluoroethyl Benzenesulfenate* (**8**). To a solution of 0.27 g (0.5 mmol) of 2,4,8,10-tetra-tert-butyl-6-(2,2,2-trifluoroethoxy)-dibenzo[d,f][1,3,2]dioxaphosphepin in 2 ml of dichloro methane-d_2 at −78°C was added a solution of 0.21 g (1 mmol) of 2,2,2-trifluoroethyl benzenesulfenate in 0.5 ml of dichloromethane-d_2. The reaction mixture was allowed to warm to room temperature and the NMR spectral data were taken immediately.

Adduct of 6-(*2,2,2-Trifluoroethoxy*)-*Dibenzo*[*d,g*][*1,3,2*]*dioxaphosphepin With Two Moles of 2,2,2-Trifluoroethyl Benzenesulfenate* (**9**). To a stirred solution of 2.25 g (7.0 mmol) of 6-(2,2,2-trifluoroethoxy)dibenzo[d,f][1,3,2]dioxaphosphepin in 30 ml of dichloromethane at −78°C was added a solution of 3.0 g (14.0 mmol) of 2,2,2-trifluoroethyl benzenesulfenate in 5 ml of the same solvent. The reaction mixture was allowed to warm to room temperature and it was stirred for one hour. The reaction mixture was cooled to −70°C and the solid was removed by filtration. The filtrate was concentrated *in vacuo* and the residual oil was molecularly distilled, 50°C (block), 0.01 mm, to yield 1.3 g (41%) of **9**.

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