Synthesis and Structure of Cyclic Phosphate, Phosphoramidate, Phosphonates, and Phosphonium Salts. Phosphatrane Formation[1]

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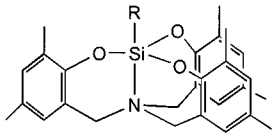
Reaction of tris(2-hydroxy-3,5-dimethylbenzyl)amine (**6**) with phosphorus reagents led to the formation of the phosphoramidate, $N[CH_2(Me_2C_6H_2)O]_2PO$ (**1**), the phosphate $N[CH_2(Me_2C_6H_2)O]_2[CH_2(Me_2C_6H_2)OH]P(O)(OPh)$ (**2**), the phosphonium salts $N[CH_2(Me_2C_6H_2)O]_3PMe^+I^-$ (**3A**) and $N[CH_2(Me_2C_6H_2)O]_3PMe^+I_3^-$ (**3B**), and the phosphonates $N[CH_2(Me_2C_6H_2)O]_2[CH_2(Me_2C_6H_2)OH]P(O)Me$ (**4**) and $N[CH_2(Me_2C_6H_2)O]_2[CH_2(Me_2C_6H_2)OSiMe_3]P(O)Me$ (**5**). X-ray analysis provided molecular structures for all of the compounds. The solid-state structural representations were supported in solution by an analysis of the NCH_2 proton NMR patterns. The structures of **3A** and **3B** show the presence of phosphatranes with weak P−N donor interactions. These represent the first phosphatranes containing all six-membered rings. Variable temperature analysis of the ^1H NMR spectra of **3A** indicates fluxional behavior whereby a racemic mixture of the chiral phosphonium salt rapidly intraconverts at room temperature. The activation energy for the enantiomeric conversion of the clockwise and anticlockwise orientations of the propeller-like phosphatrane is 11.2 kcal/mol, which is compared to that of the isoelectronic silatrane $N[CH_2(Me_2C_6H_2)O]_3SiMe$ (**E**), 10.3 kcal/mol.

Introduction

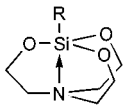
Recently, we prepared and structurally characterized a new class of silatranes[2] with tricyclic rings that contain all six-membered rings. All previous work in silatrane chemistry contain at least two five-membered rings and most are composed entirely of five-membered rings.[3] We have shown that due to the greater rigidity imposed by the use of five-membered rings, the nitrogen−silicon distance is confined to a narrow range when substitutional variations are introduced. The $Si-N_{ax}$ transannular interaction generally falls in the range of 2.0−2.3 Å,[3] whereas with tricyclic six-membered rings, on a more limited sample that we studied, the range varied over 0.7 Å from 2.03 to 2.75 Å.[2] In fact, when the comparison was made with a common set of substituents in the trans apical position, the range for the silatranes with five-membered rings **A**−**D** was confined to 2.03−2.19 Å[4−7] compared to the 2.03−2.75 Å range for the silatranes with all six-membered rings, **E**−**H** (Table 1).

As with silatranes, all previous studies of phosphatranes incorporate five-membered rings into the cyclic framework.[3]

Table 1. Comparison of Silicon−Nitrogen Distances in Silatranes with Six-Membered Rings and Five-Membered Rings



E - H



A - D

six-membered				five-membered		
no.	R	SiN, Å	% TBP	no.	R	SiN, Å
E[a]	Me	2.745(4)	53	A[b]	Me	2.175(4)
F[a]	OMe	2.633(6)	59	B[c]	OEt	2.152(13)
G[a]	Ph	2.283(3)	82	C[d]	Ph[d]	2.193(5)[6a]
		2.193(3)				2.156(4)[6b]
						2.132(4)[6c]
H[a]	CCl_3	2.025(4)	95	D[e]	Cl	2.026(10)

[a] Reference 2. [b] Reference 4. [c] Reference 5. [d] Reference 6. [e] Reference 7.

The present work centers on a continuing interest we have in comparing the chemistry of silicon[8−16] and phosphorus[8−17] in similar environments, particularly with regard to donor−acceptor

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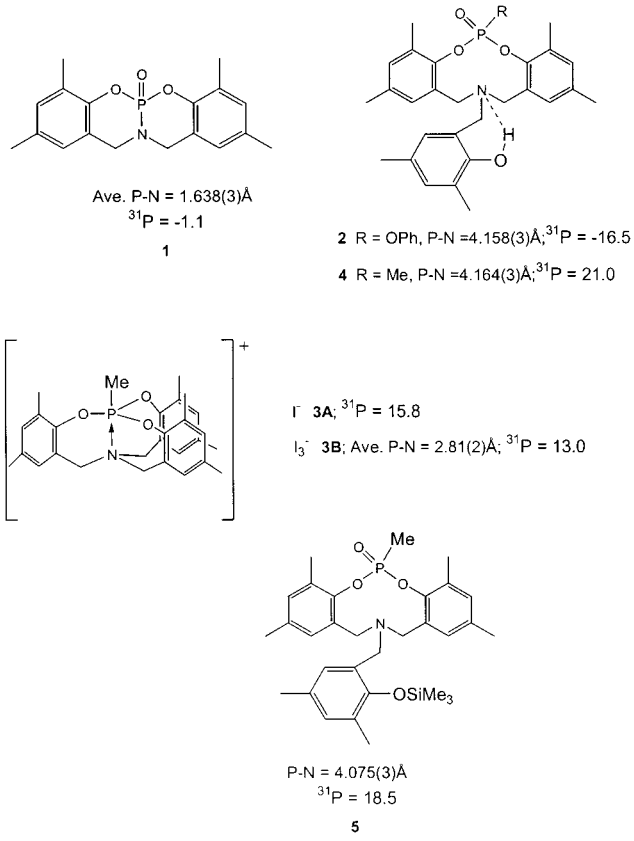
Chart 1



interactions. The same aminotriphenol that was employed in forming the silatranes **E**−**H**[2] was used in this study. A variety of products **1**−**5** resulted (Chart 1) indicative of the diverse reactions of phosphorus. X-ray analysis of all of these products showed the formation of phosphoramidate **1**, phosphate **2**, phosphonium salts **3A** and **3B**, and phosphonates **4** and **5**. The phosphonium salts, which are isoelectronic with silatrane **A**, proved to be phosphatranes and hence represent the first examples of phosphatranes containing all six-membered rings.

Experimental Section

Phosphorus oxychloride, phenoxyphosphoryl chloride, methyltriphenoxyphosphonium iodide, and hexamethyldisilazane were obtained from Aldrich and used as supplied. Triethylamine and tetramethylethylenediamine (Aldrich) were distilled over KOH pellets. Tris(2-hydroxy-3,5-dimethylbenzyl)amine (**6**) was synthesized as described earlier.[2] Solvents were purified according to the standard procedures.[18] All the reactions were carried out in a dry nitrogen atmosphere. Proton NMR spectra were recorded on a Bruker AC200 FT-NMR spectrometer, and the phosphorus-31 NMR spectra were recorded on a Bruker DPX300 FT-NMR spectrometer. All ^{1}H NMR spectra were recorded in $CDCl_3$, and all the ^{31}P NMR spectra were recorded in CH_2Cl_2 in sweep-off mode, unless mentioned otherwise. Chemical shifts are reported in parts per million, downfield positive, and relative to tetramethylsilane for ^{1}H NMR or 85% H_3PO_4 for ^{31}P NMR. All spectra were recorded at around 23 °C unless stated otherwise. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. N[CH$_2$(Me$_2$C$_6$H$_2$)O]$_2$PO (1). A solution of **6** (1.80 g, 4.29 mmol) and tetramethylethylenediamine (2.00 mL, 13.3 mmol) in dichloromethane (75 mL) was added to a solution of phosphorus oxychloride (0.400 mL, 4.29 mmol) in dichloromethane (75 mL) with stirring at room temperature over a period of 1 h. The solution was stirred for a further period of 18 h. The resulting solution was washed with 5% aqueous sodium chloride (3 × 100 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated to 40 mL and hexane (40 mL) was added. The filtrate was left under a flow of nitrogen to obtain a microcrystalline product. Yield: 1.20 g (85%); mp 145−150 °C. ^{1}H NMR: δ 2.19 (s, 6H, aryl-*Me*), 2.21 (s, 6H, aryl-*Me*), 3.88 (dd, J_{PH} = 20.2 Hz, J_{HH} = 15.5 Hz, 2H, NC*H*$_2$), 4.63 (dd, J_{HH} = 15.5 Hz, J_{PH} = 5.7 Hz, 2H, NC*H*$_2$), 6.64 (s, 2H, aryl), 6.83 (s, 2H, aryl). ^{31}P NMR: δ −1.1. Anal. Calcd for $C_{18}H_{20}NO_3P$: C, 65.65; H, 6.12; N, 4.25. Found: C, 65.44; H, 6.49; N, 4.35.

N[CH$_2$(Me$_2$C$_6$H$_2$)O]$_2$[CH$_2$(Me$_2$C$_6$H$_2$)OH]P(O)(OPh) (2). A solution of **6** (2.80 g, 6.67 mmol) and tetramethylethylenediamine (2.00 mL, 13.3 mmol) in dichloromethane (75 mL) was added to a solution of phenoxyphosphoryl chloride (1.00 mL, 6.69 mmol) in dichloromethane (75 mL) with stirring at −60 °C over a period of 40 min. The solution was allowed to come to room temperature and stirred for a further period of 19 h. The solvent was removed, the residue extracted with ether (150 mL), filtered, and the solvent removed. Attempts to crystallize the pasty mass from hexane−dichloromethane (1:1, 80 mL) and from hot toluene (40 mL) were not successful. The pasty mass was dissolved in hot methanol (40 mL) and left aside in the open atmosphere overnight to obtain needle crystals of the expected compound. Yield: 0.85 g (23%); mp 171−174 °C. ^{1}H NMR: δ 2.16 (s, 6H, aryl-*Me*), 2.21 (s, 3H, aryl-*Me*), 2.23 (s, 9H, aryl-*Me*), 3.67 (s, 2H, NC*H*$_2$), 3.87 (s, 2H, NC*H*$_2$), 3.89 (s, 2H, NC*H*$_2$), 6.51 (s, 1H, aryl), 6.77 (s, 2H, aryl), 6.88 (s, 1H, aryl), 6.93 (s, 2H, aryl), 7.40 (m, 5H, aryl). ^{31}P NMR: −16.5. Anal. Calcd for $C_{33}H_{36}NO_5P$: C, 71.08; H, 6.51; N, 2.51. Found: C, 70.77; H, 6.69; N, 2.45.

1-Methylphosphonium-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′,6′-dimethylbenzo) [4.4.4.0^{1,6}] tricyclotetradecane Iodide, N[CH$_2$(Me$_2$C$_6$H$_2$)O]$_3$PMe$^+$I$^-$ (3A). A solution of **6** (3.00 g, 7.15 mmol) and MeP(OPh)$_3^+$I$^-$ (3.30 g, 7.30 mmol) in dichloromethane (130 mL) was stirred for 30 min and left under a nitrogen flow. The residue was washed with ether (50 mL) and recrystallized from heptane−dichloromethane (20:80 mL) under a slow nitrogen flow. First red-brown crystals formed, and then a yellow powder started to precipitate. The solution was decanted to separate the red-brown crystalline compound. Yield: 1.50 g (27%); mp 130−140 °C. ^{1}H NMR: δ 2.28 (s, 9H, aryl-*Me*), 2.44 (s, 9H, aryl-*Me*), 2.98 (d, 16.6 Hz, 3H, PC*H*$_3$), 3.61 (s, 6H, NC*H*$_2$), 6.90 (m, 3H, phenol), 6.94 (s, 3H, aryl), 7.02 (s, 3H, aryl), 7.18 (m, 2H, phenol). ^{1}H NMR (CD_2Cl_2: 290 K): δ 2.30 (s, 9H, aryl-*Me*), 2.39 (s, 9H, aryl-*Me*), 2.78 (d, 17.0 Hz, 3H, PC*H*$_3$), 3.58 (s, 6H, NC*H*$_2$), 7.00 (m, 11H, aryl+phenol). ^{1}H NMR (CD_2Cl_2: 190 K): δ 2.30 (s, 9H, aryl-*Me*), 2.39 (s, 9H, aryl-*Me*), 2.77 (d, 16.6 Hz, 3H, PC*H*$_3$), 3.13 (d, 13.2 Hz, 3H, NC*H*$_2$), 3.91 (d, 13.2 Hz, 3H, NC*H*$_2$), 7.00 (m, 11H, aryl+phenol). ^{31}P NMR: δ 15.8 (J_{PCH} = 15.9 Hz). Anal. Calcd for $C_{28}H_{33}NO_3PI\cdot PhOH\cdot{}^1/_2CH_2Cl_2$: C, 57.08; H, 5.55; N, 1.93. Found: C, 56.30; H, 5.48; N, 1.97.

N[CH$_2$(Me$_2$C$_6$H$_2$)O]$_2$[CH$_2$(Me$_2$C$_6$H$_2$)OH]P(O)Me (4). The mother liquor from **3A** did not give any further crystalline material (^{31}P: 30.7, 26.3, 23.3, minor 17.1 ppm). To the mother liquor was added an excess of $Et_4NF\cdot xH_2O$ (2.0 g) in dichloromethane and stirred overnight during which time the solution had become colorless. The solvent was removed and the residue extracted with ether (100 mL) and filtered. The solution was left under a slow flow of nitrogen to obtain the crystalline compound **4**. Yield: 0.70 g (20%); mp 191−193 °C. ^{1}H NMR: δ 2.04 (d, 17.6 Hz, 3H, PC*H*$_3$), 2.19 (s, 3H, aryl-*Me*), 2.24 (s, 9H, aryl-*Me*), 2.35 (s, 6H, aryl-*Me*), 3.61 (s, 2H, NC*H*$_2$), 3.86 (s, 4H, NC*H*$_2$), 6.46 (s, 1H, aryl), 6.79 (s, 2H, aryl), 6.88 (s, 1H, aryl), 6.97 (s, 2H, aryl). ^{31}P NMR: δ 21.0. Anal. Calcd for $C_{28}H_{34}NO_4P$: C, 70.13; H, 7.15; N, 2.92. Found: C, 70.17; H, 7.19; N, 2.93.

1-Methylphosphonium-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris-(4′,6′-dimethylbenzo) [4.4.4.0^{1,6}] tricyclotetradecane Triiodide, N[CH$_2$(Me$_2$C$_6$H$_2$)O]$_3$PMe$^+$I$_3^-$ (3B). A solution of **6** (2.00 g, 4.77 mmol) and MeP(OPh)$_3$I (2.20 g, 4.87 mmol) in dichloromethane−heptane (100:50 mL) was stirred for 30 min and allowed to stand. After

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Table 2. Crystallographic Data for Compounds **1**−**5**

	compd **1**	compd **2**	compd **3A**	compd **3B**	compd **4**	compd **5**
formula	$C_{18}H_{20}NO_3P$	$C_{33}H_{36}NO_5P$	$C_{28}H_{33}NO_3P{\cdot}I{\cdot}PhOH{\cdot}CH_2Cl_2$	$C_{28}H_{33}NO_3P{\cdot}I_3{\cdot}CH_2Cl_2{\cdot}^1/_4PhOH$	$C_{28}H_{34}NO_4P$	$C_{33}H_{42}NO_4PSi$
formula wt	329.3	557.6	768.5	951.7	479.5	551.7
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	*C*2/*c*	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
cryst size, mm	0.30 × 0.35 × 1.00	0.25 × 0.30 × 0.65	0.25 × 0.65 × 1.50	0.60 × 0.70 × 1.00	0.45 × 0.50 × 0.70	0.50 × 0.50 × 0.75
a, Å	9.837(2)	30.412(7)	14.174(4)	14.515(5)	9.935(2)	14.998(4)
b, Å	11.168(4)	13.246(3)	14.377(4)	20.625(6)	26.418(7)	8.487(2)
c, Å	15.462(4)	14.628(3)	19.005(5)	24.177(8)	10.365(3)	25.352(6)
α, deg	86.36(2)	90	96.27(2)	90	90	90
β, deg	89.46(2)	89.69(2)	94.06(2)	93.44(3)	109.46(2)	102.55(2)
γ, deg	85.86(2)	90	106.00(2)	90	90	90
V, Å^3	1690.8(8)	5893(2)	3680(1)	7225(4)	2565(1)	3150(1)
Z	4	8	4	8	4	4
D_{calc}, g/cm^3	1.294	1.257	1.387	1.750	1.242	1.163
μ(Mo Kα), cm^{-1}	1.77	1.35	11.0	28.19	1.41	1.59
total reflns	4140	3610	8973	8832	3146	3835
reflns with $I > 2\sigma_I$	2754	2302	5786	4719	2198	2722
R[a]	0.0377	0.0472	0.16	0.0911	0.0510	0.0421
R_w[b]	0.0989	0.1087	0.44	0.2585	0.1398	0.1126

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = \{\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4\}^{1/2}$.

20 h, iodine (1.20 g, 4.73 mmol) was added and the solution stirred for 30 min. The solution was left under a slow nitrogen flow. First deep red-brown crystals formed, and then a black tarry material started to deposit. The solution was decanted, and the crystals were removed with a spatula. Yield: 0.40 g (9%); mp 177−182 °C. ^{1}H NMR: δ 2.32 (s, 9H, aryl-*Me*), 2.44 (s, 9H, aryl-*Me*), 2.83 (d, 17.0 Hz, 3H, PC*H*$_3$), 3.67 (s, 6H, NC*H*$_2$), 7.00 (s, 3H, aryl), 7.07 (s, 3H, aryl), 6.90 (m, $^3/_4$H, phenol), 7.18 (m, $^1/_2$H, phenol). ^{31}P NMR: δ 13.0.

The mother liquor from **3B** did not give any further crystalline material. The mother liquor was dissolved in methanol (50 mL), and excess Et_3N (4.0 mL) was added. The solution was left overnight which afforded crystals of **4**. Yield: 1.0 g (44%).

N[CH$_2$(Me$_2$C$_6$H$_2$)O]$_2$[CH$_2$(Me$_2$C$_6$H$_2$)OSiMe$_3$]P(O)Me (5). A mixture of **4** (0.700 g, 1.46 mmol) and excess of hexamethyldisilazane (2.00 mL, 9.48 mmol) was heated at reflux for 1 h. The mixture was washed with heptane (20 mL), dissolved in heptane−dichloromethane (30:30 mL), and left under a nitrogen flow to obtain a crystalline product. Yield: 0.55 g (68%); mp 156−159 °C. ^{1}H NMR (DPX300): δ 0.11 (s, 9H, SiMe$_3$), 1.96 (d, 17.7 Hz, 3H, PC*H*$_3$), 2.15 (s, 3H, aryl-*Me*), 2.17 (s, 3H, aryl-*Me*), 2.20 (s, 6H, aryl-*Me*), 2.38 (s, 6H, aryl-*Me*), 3.50 (s, 2H, NC*H*$_2$), 3.67 (d, J_{HH} = 13.2 Hz, 2H, NC*H*$_2$), 4.63 (d, J_{HH} = 13.2 Hz, 2H, NC*H*$_2$), 6.73 (s, 2H, aryl), 6.75 (s, 1H, aryl), 6.89 (s, 2H, aryl), 7.12 (s, 1H, aryl). ^{31}P NMR: δ 18.5 Anal. Calcd for $C_{31}H_{42}NO_4PSi$: C, 67.49; H, 7.67; N, 2.54. Found: C, 68.12; H, 7.67; N, 2.62.

X-ray Studies. The X-ray crystallographic studies were performed using an Enraf-Nonius CAD4 diffractometer and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Details of the experimental procedures have been described previously.[19]

The colorless crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected at 23 ± 2 °C using the $\theta-2\theta$ scan mode with 4° ≤ $2\theta_{MoK\alpha}$ ≤ 44°. No corrections were made for absorption. An absorption correction applied to **3B** using 13 psi data (T_{min}/T_{max} = 0.56) resulted in bad atomic displacement parameters including one negative value. Hence, the corrected data were not used. All of the data with positive intensities were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by the full-matrix least-squares method. Refinements were based on F^2, and computations were performed on a 486/66 computer using SHELXS-86 for solution[20] and SHELXL-93 for refinement.[21] All the non-hydrogen atoms, except those of solvents, were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding either in ideal positions or with torsional refinement (in the case of methyl and hydroxyl hydrogen atoms) on the bonded atoms. The final agreement factors are based on the reflections with $I > 2\sigma_I$. Crystallographic data are summarized in Table 2.

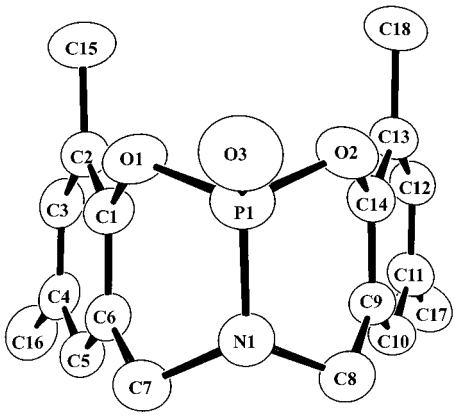

Figure 1. ORTEX diagram of the phosphoramidate N[CH$_2$(Me$_2$-C$_6$H$_2$)O]$_2$PO (**1**).

In crystals of **1**, **3A**, and **3B**, there were two molecules in each asymmetric unit. The structure of **3A** could not be fully completed due to the poorly behaved solvent molecules (two phenols and some dichloromethane molecules with partial occupancies). The data were collected three times using different crystals, but the problem remained the same, and hence **3B** was synthesized to obtain complete information. However the main part of the structure for **3A** was easily obtained and was essentially similar to that of **3B**. In **3B** also there were two molecules of dichloromethane and a half molecule of phenol (positioned at an inversion center) in each asymmetric unit, but all were well-behaved. The oxygen atom for the phenol was refined with half-occupancy due to disordered packing, and the hydrogens of the solvents were not included in the calculations.

Results and Discussion

The atom-labeling schemes for **1**−**5** are given in the ORTEX[22] plots of Figures **1**−**5**. The thermal ellipsoids are shown at the 40% probability level, and all hydrogens are omitted for clarity. Selected bond parameters are given in Tables 3−7.

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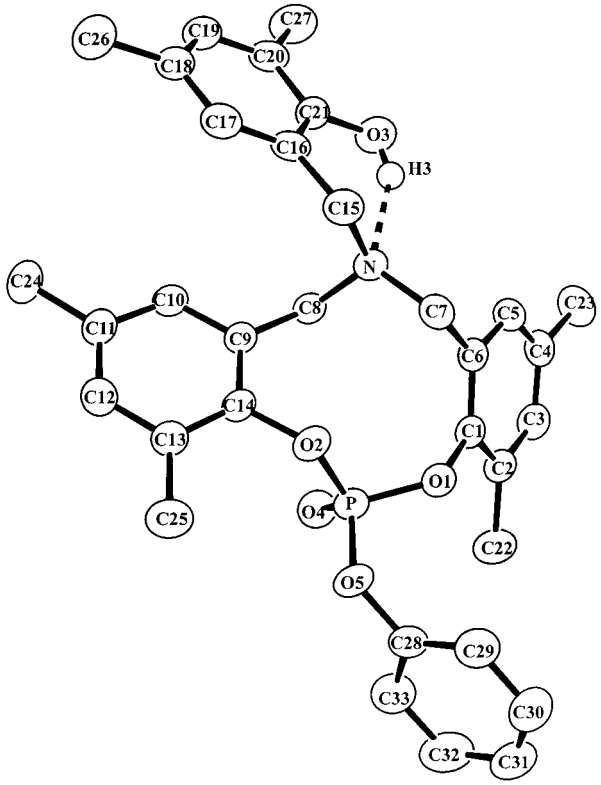


Figure 2. ORTEX diagram of the phosphate $N[CH_2(Me_2C_6H_2)O]_2$-$[CH_2(Me_2C_6H_2)OH]P(O)(OPh)$ (**2**).

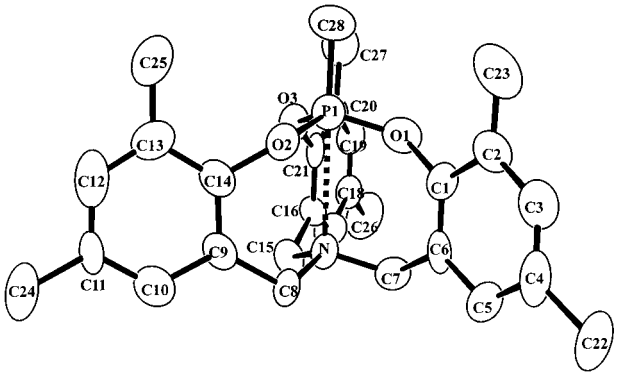


Figure 3. ORTEX diagram of the phosphonium-atrane $N[CH_2(Me_2C_6H_2)O]_3PMe^+I_3^-$ (**3B**). The solvent molecules of crystallization and the triiodide anion have been omitted.

Syntheses. Scheme 1 outlines the synthetic pathways for the formation of **1**−**5** resulting from the use of tris(2-hydroxy-3,5-dimethylbenzyl)amine (**6**) as the coupling ligand. The variety of products obtained contrasts with reactions of organosilanes or tetramethyl orthosilicate with the same coupling amine (**6**), which led to the silatranes **E**−**H**[2] listed in Table 1. This occurrence is most likely due to the presence of the phosphoryl group which negates the formation of an additional P−O bond to give the tricyclic derivative. This is indicated by the formulations for the phosphoramidate **1**, the phosphate **2**, and the phosphonates **4** and **5**. The phosphonium-atranes **3A** and **3B** were synthesized by a trans-esterification reaction with methyltriphenoxyphosphonium iodide. The phosphatranes **3A** and **3B** on hydrolysis readily form the phosphoryl group in yielding the phosphonate **4**. In **4**, the nitrogen atom is involved in hydrogen bonding with the hydroxyl proton, OH = 0.82 Å (fixed), H···N = 1.96 Å, and O−H···N = 146°. This is similar to the hydrogen bond present in the closely related compound **2**, OH = 0.82 Å (fixed), H···N = 2.03 Å, and O−H···N = 146°. The hydroxyl group of **4** was derivatized to exclude the hydrogen bonding possibility and to allow the possibility of formation of a P−N interaction. However, despite the avail-

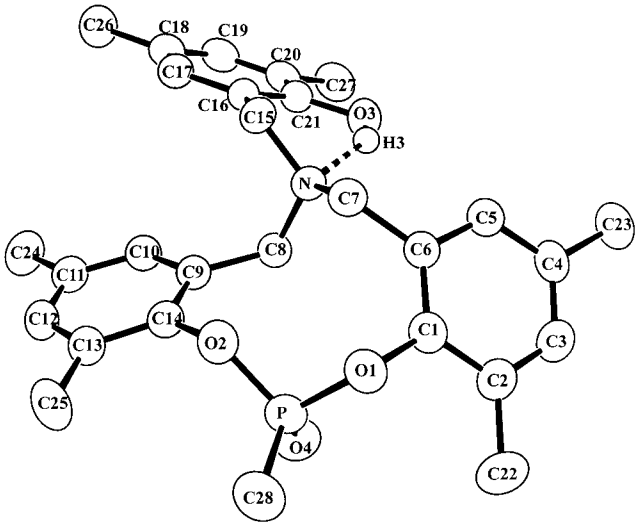


Figure 4. ORTEX diagram of the phosphonate $N[CH_2(Me_2C_6H_2)O]_2$-$[CH_2(Me_2C_6H_2)OH]P(O)Me$ (**4**).

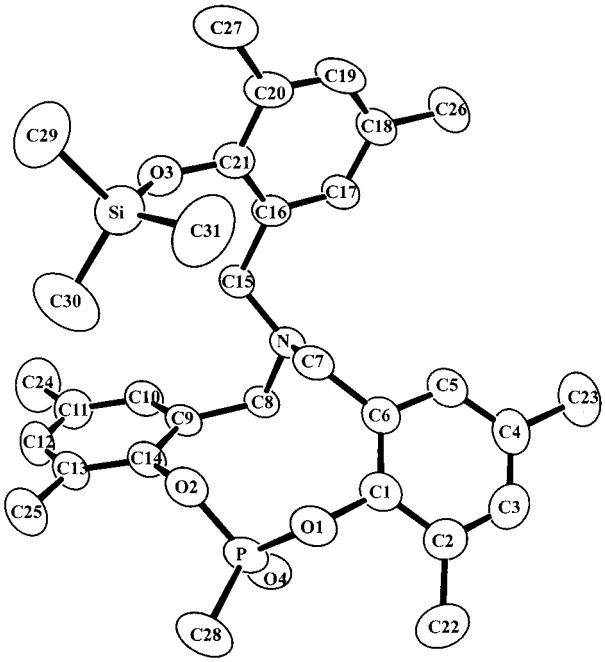


Figure 5. ORTEX diagram of the phosphonate $N[CH_2(Me_2C_6H_2)O]_2$-$[CH_2(Me_2C_6H_2)OSiMe_3]P(O)Me$ (**5**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**

P(1)−O(3)	1.453(2)	P(2)−O(3A)	1.451(2)
P(1)−O(1)	1.584(2)	P(2)−O(2A)	1.582(2)
P(1)−O(2)	1.583(2)	P(2)−O(1A)	1.584(2)
P(1)−N(1)	1.642(3)	P(2)−N(2)	1.634(3)
O(3)−P(1)−O(1)	110.10(13)	O(3A)−P(2)−O(2A)	110.02(13)
O(3)−P(1)−O(2)	109.86(13)	O(3A)−P(2)−O(1A)	109.66(14)
O(1)−P(1)−O(2)	106.95(12)	O(2A)−P(2)−O(1A)	106.63(12)
O(3)−P(1)−N(1)	119.81(13)	O(3A)−P(2)−N(2)	120.05(14)
O(1)−P(1)−N(1)	104.51(12)	O(2A)−P(2)−N(2)	104.86(13)
O(2)−P(1)−N(1)	104.80(13)	O(1A)−P(2)−N(2)	104.75(12)
C(1)−O(1)−P(1)	121.4(2)	C(1A)−O(1A)−P(2)	121.0(2)
C(14)−O(2)−P(1)	121.0(2)	C(14A)−O(2A)−P(2)	121.5(2)
C(7)−N(1)−C(8)	116.0(2)	C(8A)−N(2)−C(7A)	115.5(3)
C(7)−N(1)−P(1)	115.8(2)	C(8A)−N(2)−P(2)	116.3(2)
C(8)−N(1)−P(1)	116.5(2)	C(7A)−N(2)−P(2)	116.8(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **2**

P−O(4)	1.438(3)	P−O(1)	1.569(3)
P−O(2)	1.563(3)	P−O(5)	1.573(3)
O(4)−P−O(2)	115.7(2)	C(1)−O(1)−P	124.0(2)
O(4)−P−O(1)	116.3(2)	C(14)−O(2)−P	125.6(2)
O(2)−P−O(1)	103.2(2)	C(28)−O(5)−P	121.9(3)
O(4)−P−O(5)	118.3(2)	C(15)−N−C(7)	111.1(3)
O(2)−P−O(5)	100.1(2)	C(15)−N−C(8)	114.1(3)
O(1)−P−O(5)	100.5(2)	C(7)−N−C(8)	115.4(3)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **3B**

P(1)−O(1)	1.518(13)	P(2)−O(1′)	1.572(12)
P(1)−O(2)	1.572(12)	P(2)−O(2′)	1.530(12)
P(1)−O(3)	1.539(12)	P(2)−O(3′)	1.538(12)
P(1)−N(1)	2.82(2)	P(2)−N(2)	2.80(2)
P(1)−C(28)	1.75(2)	P(2)−C(28′)	1.74(2)
I(1)−I(2)	2.892(3)	I(4)−I(5)	2.827(3)
I(2)−I(3)	2.897(3)	I(5)−I(6)	3.039(3)
I(3)−I(4)	3.550(3)		
O(1)−P(1)−O(3)	114.1(7)	O(2)−P(2)−O(3)	111.8(7)
O(1)−P(1)−O(2)	114.1(6)	O(2)−P(2)−O(1)	113.1(7)
O(3)−P(1)−O(2)	111.3(7)	O(3)−P(2)−O(1)	114.4(6)
O(1)−P(1)−C(28)	104.6(9)	O(2)−P(2)−C(28)	105.4(9)
O(3)−P(1)−C(28)	106.2(8)	O(3)P(2)−C(28)	106.4(9)
O(2)−P(1)−C(28)	105.5(8)	O(1)−P(2)−C(28)	104.8(9)
O(1)−P(1)−N(1)	74.4(5)	O(2)P(2)−N(2)	74.9(6)
O(3)−P(1)−N(1)	75.1(6)	O(3)−P(2)−N(2)	74.3(5)
O(2)−P(1)−N(1)	74.2(5)	O(1)−P(2)−N(2)	74.1(6)
C(28)−P(1)−N(1)	178.7(8)	C(28)P(2)−N(2)	178.9(8)
C(1)−O(1)−P(1)	131.3(10)	C(1)ñO(1)−P(2)	130.3(10)
C(14)−O(2)−P(1)	129.5(10)	C(14)−O(2)−P(2)	132.8(10)
C(21)−O(3)−P(1)	131.7(10)	C(21)−O(3)−P(2)	129.1(10)
C(7)−N(1)−C(15)	114.5(13)	C(15)−N(2)−C(8)	113.7(14)
C(7)−N(1)−C(8)	110.5(13)	C(15)−N(2)−C(7)	109.7(13)
C(15)−N(1)−C(8)	110.2(13)	C(8)−N(2)−C(7)	110.1(13)
C(7)−N(1)−P(1)	106.5(10)	C(15)−N(2)−P(2)	107.6(10)
C(15)−N(1)−P(1)	107.6(10)	C(8)−N(2)−P(2)	107.3(11)
C(8)−N(1)−P(1)	107.2(9)	C(7)−N(2)−P(2)	108.1(10)
I(1)−I(2)−I(3)	175.07(11)	I(5)−I(4)−I(3)	171.06(8)
I(2)−I(3)−I(4)	159.31(13)	I(4)−I(5)−I(6)	175.49(8)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **4**

P−O(2)	1.595(3)	P−O(4)	1.452(3)
P−O(1)	1.578(3)	P−C(28)	1.760(4)
O(1)−P−O(2)	101.2(2)	C(14)−O(2)−P	127.3(2)
O(4)−P−O(2)	114.2(2)	C(1)−O(1)−P	125.3(2)
O(4)−P−O(1)	116.0(2)	C(7)−N−C(8)	115.3(3)
O(2−P−C(28)	106.1(2)	C(7)−N−C(15)	112.6(3)
O(1)−P−C(28)	100.2(2)	C(8)−N−C(15)	113.8(3)
O(4)−P−C(28)	117.1(2)		

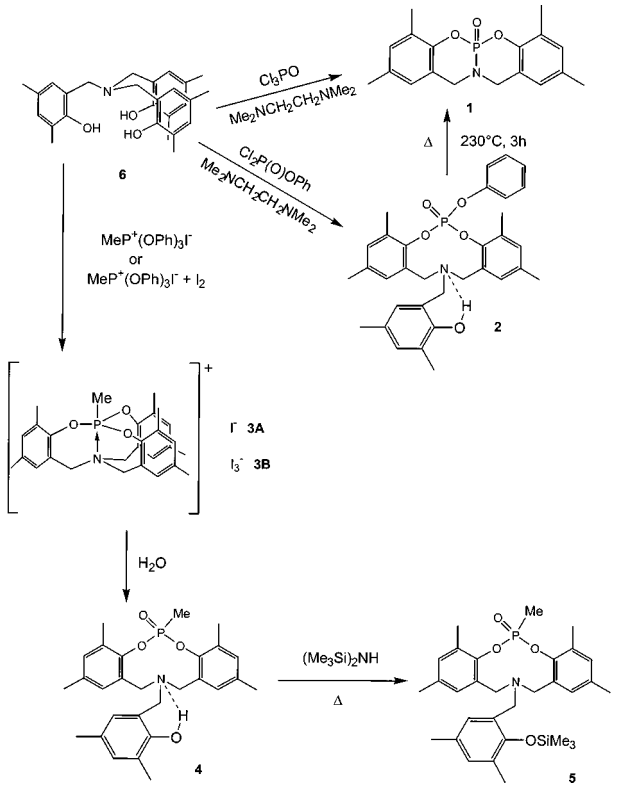
Table 7. Selected Bond Lengths (Å) and Angles (deg) for **5**

P−O(1)	1.586(2)	Si−O(3)	1.649(3)
P−O(2)	1.587(2)	Si−C(29)	1.845(4)
P−O(4)	1.452(2)	Si−C(30)	1.843(5)
P−C(28)	1.763(3)	Si−C(31)	1.843(5)
O(2)−P−O(1)	100.96(12)	O(3)−Si−C(29)	108.6(2)
O(4)−P−O(1)	115.36(13)	O(3)−Si−C(30)	107.9(2)
O(4)−P−O(2)	114.88(13)	O(3)−Si−C(31)	109.3(2)
O(1)−P−C(28)	102.2(2)	C(29)−Si−C(30)	108.7(3)
O(2)−P−C(28)	105.8(2)	C(29)−Si−C(31)	111.3(2)
O(4)−P−C(28)	115.8(2)	C(31)−Si−C(30)	111.0(3)
C(1)−O(1)−P	122.9(2)	C(7)−N−C(8)	114.7(2)
C(14)−O(2)−P	125.5(2)	C(15)−N−C(7)	112.2(2)
C(21)−O(3)−Si	132.5(2)	C(15)−N−C(8)	112.8(2)

ability of the nitrogen lone pair, no P−N interaction occurred in **5**. The P−N distance for **5** is 4.075(3) Å, much greater than the van der Waals sum.[23]

(23) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Scheme 1



In an attempt to form a phosphate-atrane by the reaction of the amine coupling agent **6** with Cl_3PO, the reaction proceeded with the cleavage of an N−C bond to give the phosphoramidate **1** instead. This occurred whether the reaction was carried out at room temperature or at −60 °C. In another attempt to form a phosphate-atrane, phosphate **2** was prepared as a precursor. However, on heating **2** to 230 °C for 3 h, quantitative conversion to **1** takes place instead of the formation of the desired atrane.

Structure. Satisfactory X-ray analysis of **1, 2, 3B, 4,** and **5** and comparisons with related structures allows us further insight about the problem of forming phosphatranes with all six-membered rings starting with the encapsulating amine **6** (Scheme 1).

Phosphate **2** and phosphoramidates **4** and **5** have closely related structures as noted by comparing Figures 2, 4, and 5. They all lack P−N coordination. The P−N distances are 4.158(3) Å for **2**, 4.164(3) Å for **4**, and 4.075(3) Å for **5**, far exceeding the sum of the van der Waals radii of 3.40 Å.[23]

The structures of these compounds may be compared to related structures of silane **I**[14] and phosphine **J**.[24] Both exhibit some measure of donor interaction with the nitrogen atom. The Si−N distance for **I** is 3.191(2) Å, and the P−N distance in **J** is 3.152(3) Å, considerably smaller than the van der Waals sum of 3.65 Å for **I** and 3.40 Å for **J**, respectively.[23] On the basis of these distances relative to the covalent sum[25]and van der Waals sum,[23] a displacement of 27% toward a trigonal bipyramid (TBP) for **I** and 24% for **J** is determined. The sum of the covalent radii used was 1.93 Å for Si−N and 1.85 Å for P−N.[25] The lack of occurrence of any P−N interaction in **2**, **4**, and **5** is reasonably associated with the presence of the phosphoryl

(24) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 4945.

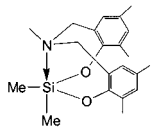
(25) Sutton, L., Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Special Publication Nos. 11 and 18; The Chemical Society: London, 1958 and 1965.

Table 8. Proton NMR Signals (ppm) and Coupling Constants (Hz) for NCH_2 Groups of **1**−**5**[a]

no.	NCH_2		
1	3.88 (2H) (dd J_{PH} = 20.2, J_{HH} = 15.5)		4.63 (2H) (dd J_{HH} = 15.5, JPH = 5.7)
3A	3.61 (6H)		
3A[b]	3.58 (6H)		
3A[c]	3.13 (3H) (d, J_{HH} = 13.2)	3.91 (3H) (d, J = 13.2)	
3B	3.67 (6H)		
2	3.67 (2H)	3.87 (2H)	2.89 (2H)
4	3.61 (2H)	3.86 (4H)	
5	3.50 (2H)	3.67 (2H) (d, J_{HH} = 13.2)	4.63 (2H) (d, J_{HH} = 13.2)

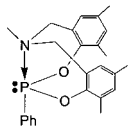
[a] All ^{1}H NMR spectra were obtained at 23 °C from $CDCl_3$ solutions except for **3A** noted in footnotes *b* and *c*. [b] Recorded at +23 °C in CD_2Cl_2. [c] Recorded at −83.2 °C in CD_2Cl_2.

group, which due to its π back-bonding ability reduces the electrophilicity at phosphorus compared to the higher Lewis acidity expected in **H** and **I**.



Si-N = 3.191(2)Å

I



P-N = 3.152(3)Å

J

When the phosphoryl group in the initial phosphorus reagent is replaced by a methyl group, the amine ligand **6** with its three oxygen atoms fully encapsulates the phosphorus atom and allows nitrogen donor action to occur in forming the phosphonium-atranes **3A** and **3B**. The average P−N distance, 2.81(2) Å for **3B,** is smaller than the van der Waals sum[23] by 0.34 Å. This amounts to a displacement toward a TBP geometry of about 38%. Due to poorly behaved solvent molecules, the X-ray analysis of **3A** could not be completed. However, the main skeleton of the phosphonium-atrane was readily solved, which is similar to **3B** for which the structure was obtained.

It is interesting that the silatrane **E** that we recently reported,[2] which is isoelectronic with the phosphonium cations **3A** and **3B**, is displaced 53% toward a TBP on the basis of its Si−N distance of 2.745(4) Å (Table 1). It might be expected that **3B** would be more strongly coordinated than the silatrane **E** due to a nuclear charge effect. The reason for this is not apparent at present.

NMR Spectroscopy. The proton NMR data are most instructive in indicating that structural integrity is maintained in solution relative to that obtained from X-ray analysis (Figures 1−5). ^{31}P chemical shifts as shown in Chart 1 do not provide a meaningful variation over the series of compounds **1**−**5**. The range is −1.1 to +21.0 ppm within which is the shift for the phosphatranes **3A** and **3B**. The latter shifts do not reflect the presence of a P−N interaction, which is the situation usually found when weak donor action prevails.[8−17]

Table 8 lists the proton resonances of the NCH_2 groups along with the number of protons responsible for each signal. Also any coupling constants that were obtained are listed.

Phosphoramidate **1** exhibits two NCH_2 proton resonances. One signal is assigned to a proton from each NCH_2 group having the same spatial orientation which differs from that of the other set of two NCH_2 protons. P−NCH_2 proton spin coupling is present as well as proton−proton coupling between the protons of the same NCH_2 group. Thus, the presence of the strong P−N bond (1.638(3) Å) is preserved in solution.

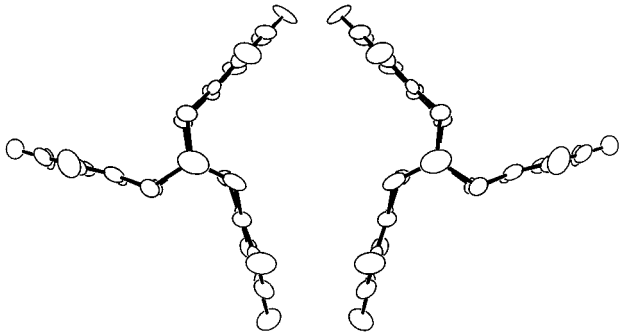


Figure 6. ORTEX diagram showing the clockwise and anticlockwise orientations of chiral centrosymmetric related molecules of **3A**. Both are viewed along the Me−P−N axis with Me at the top.

For the phosphate **2**, three resonances are present for the NCH_2 protons which is consistent with the solid-state structure shown in Figure 2. Like **1**, two sets of protons are associated with the NCH_2 groups in the ring formation, while the third signal is assignable to the NCH_2 protons of the pendant group. The structures of phosphonates **4** and **5,** which are closely related to **2,** show similar NCH_2 proton spectra, although in the case of **4**, the signal at 3.86 ppm represents four protons. In **2**, these proton signals were very close together and apparently not resolved for **4**. Phosphonate **5** does show proton−proton coupling which suggests the two signals having these couplings are associated with the two sets of protons of the NCH_2 groups which are part of the ring formulation, similar to that discussed for **1**. Unlike **1**, no P−H spin coupling is present, which is consistent with the lack of any phosphorus−nitrogen interaction. The solid-state structures (Figures 2, 4, and 5 and Chart 1) have P−N distances that all exceed 4 Å and thus are outside the range for any P−N donor interaction.

The phosphonium-atranes **3A** and **3B** are unique in the present series. Both show only one type of NCH_2 proton at 23 °C. On cooling **3A** to −83.2 °C, however, coalescence and separation into two signals of equal intensity occur. The signals as with **1** are assignable to two sets of protons, one set from a proton on each of three NCH_2 groups and a second set from the other three NCH_2 protons. No P−N−CH_2 spin coupling is present, which is common for structures exhibiting modest P−N donor interaction,[8−17] as noted here (Figure 3). The proton coupling observed is assigned to proton−proton coupling between the two sets. The magnitude (J_{HH} = 13.2 Hz) is the same as that found for **5** that exists without any P−N interaction.

An activation energy ($\Delta G^{\ddagger}$) for proton exchange for **3A** of 11.2 kcal/mol was calculated[26] on the basis of a coalescence temperature of 240 K and a line separation of 158 Hz. The proton exchange behavior is entirely analogous to that which we reported for the series of silatranes, **E**−**H**.[2] The activation energies for this series were within experimental uncertainty of each other and averaged 10 kcal/mol.

The temperature-dependent solution NMR data for **3A** indicate the presence of a racemic mixture of the chiral phosphonium-atrane that rapidly intraconverts at room temperature. This process can be visualized relative to the propeller arrangement for these molecules, as displayed in Figure 6. The three rings most likely flip or pseudorotate simultaneously to

(26) The activation energies $\Delta G^{\ddagger}$ also listed were calculated from $\Delta G^{\ddagger} = (4.57 \times 10^{-3})\ T_c\ (10.32 + \log(T_c\sqrt{2}/\pi\Delta\nu))$ as described by: Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; McGraw-Hill: New York, 1989; p 103.

cause the clockwise and counterclockwise propeller orientations to interchange with one another similiar to that advanced for exchange behavior of the silatranes.[2] Whether P−N interaction persists during this process is inconsequential.

Summary and Conclusion

Reactions carried out with tris(2-hydroxy-3,5-dimethylbenzyl)amine and phosphorus compounds revealed a variety of products, **1**−**5**, suggesting that the formation of phosphatranes containing all six-membered rings are more difficult to obtain compared with the formation of analogous silatranes, **E**−**H**, from the same reactant. However, the formation of the chiral phosphonium-atrane **3** showed structural similarity to the isoelectronic silatrane **E**. In addition, the fluxional behavior of the phosphatrane showed entirely analogous behavior to the silatranes, both with respect to activation energies for intraconversion of enantiomers and the mechanism of intraconversion involving a propeller-like rearrangement of the cyclic components of the ring systems.[2]

Acknowledgment. The support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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