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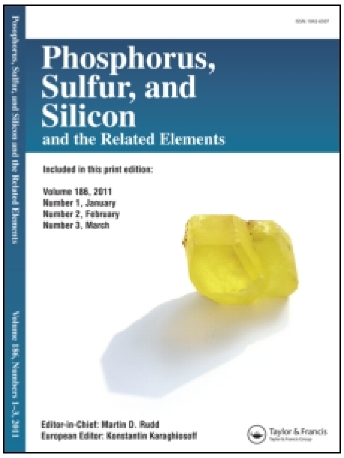

Phosphorus, Sulfur, and Silicon and the Related Elements

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The Effect of Very Bulky Groups on the Equilibrium of Penta- and Hexacoordinated Phosphoranes[1]

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The Effect of Very Bulky Groups on the Equilibrium of Penta- and Hexa-coordinated Phosphoranes[1]

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*The synthesis of dithio-diphenol **4** and sulfonyl-diphenol **5**, both with very bulky groups, provided starting materials for reaction sequences that led to the formation of the very stable hexacoordinated phosphorane **2** and sensitive pentacoordinated phosphorane **3**. Hexacoordination was established in **2** by an intramolecular donor interaction at the phosphorus center from an oxygen atom of the sulfonyl group present as part of the eight-membered ring. The solid state structures of **2** and **3** were established by X-ray analysis, as was that of phosphite **1** formed in the reaction sequence leading to **2**. In solution, **2** has two forms existing in a dynamic equilibrium between a pentacoordinated and the more dominant hexacoordinated form as determined by ^{31}P and ^{19}F NMR spectroscopy. The high stability of **2** with respect to hydrolysis and alcoholysis reactions suggests that an associative process is responsible as the controlling reaction mechanism.*

Keywords Cyclic sulfonyl derivatives; hexacoordination; phosphoranes; steric effects; X-ray crystallography

INTRODUCTION

In recent work, we presented hypervalent phosphorus chemistry and the importance of penta- and hexacoordinated phosphorus in the phosphoryl transfer enzymes in *Accounts of Chemical Research* articles[2] and in a keynote lecture (at the 7th International Conference on Heteroatom Chemistry).[3] The ease with which phosphorus isomerizes between a

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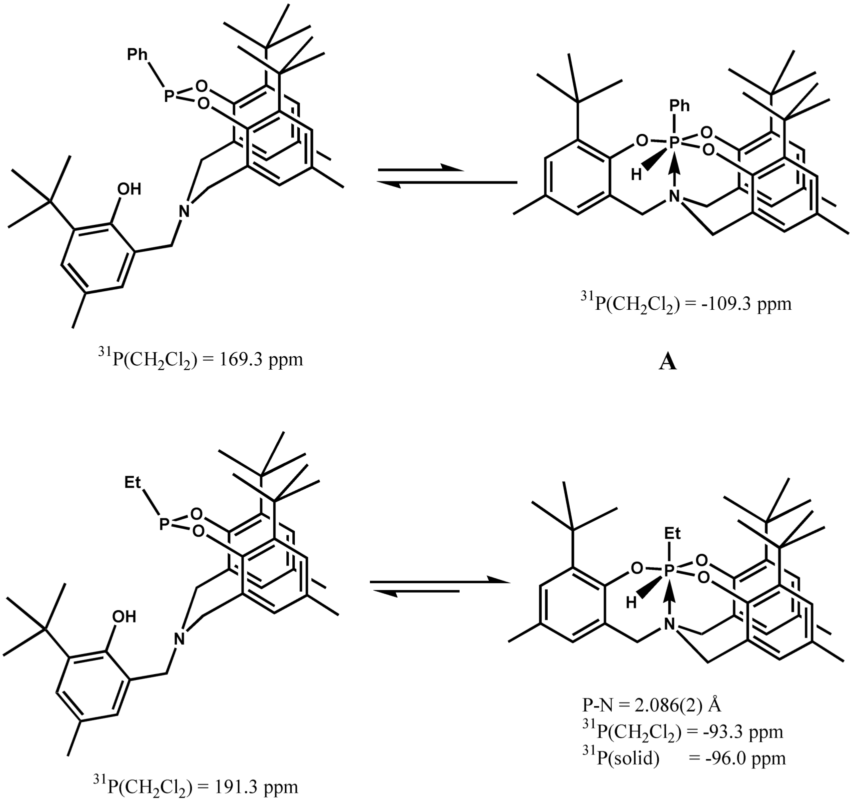
trigonal bipyramid and an octahedral geometry was emphasized. Also, we had reported a new class of atranes containing phosphorus that equilibrated between three and six coordinated states in solution. Both coordinate forms were confirmed by crystallographic studies (Scheme 1).[4]



$^{31}P(CH_2Cl_2) = 169.3$ ppm

$^{31}P(CH_2Cl_2) = -109.3$ ppm

A

$^{31}P(CH_2Cl_2) = 191.3$ ppm

P-N = 2.086(2) Å
$^{31}P(CH_2Cl_2) = -93.3$ ppm
$^{31}P(solid) = -96.0$ ppm

B

SCHEME 1

In phosphoranes containing the sulfonyl group, we had reported the ease with which phosphorus can go from five coordination to six coordination.[5,6] In the latter penta-hexa coordinate equilibrium, we observed only the pentacoordinated phosphorane in the solid state, but the nature and strength of the hexacoordinated form remained unknown. To investigate this problem more extensively, we synthesized new diphenols consisting of very bulky groups. Employing these diphenols in new reaction sequences, we were able to stabilize the phosphorane in its hexacoordinated state and obtain its crystal structure. Herein we report the synthesis of two of these new bulky diphenols and their phosphorus derivatives along with their solution NMR behavior. In addition, details of the crystallographic studies of the phosphorus derivatives are reported.

EXPERIMENTAL SECTION

2,4-bis(α,α-dimethylbenzyl)phenol (Aldrich) was used as supplied, whereas trifluoroethanol (Fluka) was dried over molecular sieves (4 Å, flame-dried under vacuum). Sulfur dichloride (80%, Aldrich) was purified according to literature method.[7] N-chlorodiisopropylamine[6] was synthesized according to our earlier methods. Solvents were purified according to standard procedures.[8] All reactions were carried out in an argon atmosphere. Solution NMR spectra were recorded on a Bruker Avance-400 (^{1}H and ^{31}P at 400.1 and 162.0 MHz, respectively) or a Bruker DPX300 FT NMR (^{19}F at 282.4 MHz) spectrometer. Solution phosphorus NMR spectra were recorded in a sweep-off mode. Chemical shifts are reported in ppm, are downfield positive and relative to tetramethylsilane for ^{1}H and $CFCl_3$ for ^{19}F NMR and 85% H_3PO_4 for ^{31}P NMR. All were recorded at around 23°C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory, Amherst, MA.

Syntheses

$O_2S[C_6H_2(CMe_2Ph)_2O]_2P(OCH_2CF_3)$ (1)

Diphenol 5 (8.3 g, 11.5 mmol) and phosphorus trichloride (1.00 mL, 11.5 mmol) were stirred in dichloromethane (100 mL). Triethylamine (5.00 mL, 35.9 mmol) was added dropwise over a period of 20 minutes, and the solution was stirred further for 2 h. Trifluoroethanol (0.90 mL, 12.3 mmol) was added, and the reaction mixture was stirred for 24 h. The solvent was removed by distillation, and the residue was extracted with ether (150 mL) and filtered, and the solvent was removed. The resultant paste was stirred with heptane (50 mL) to obtain a powdery solid. The solid was filtered, washed with heptane (2 × 20 mL), and dried. Yield 8.10 g (83%). Single crystals suitable for an X-ray study were obtained from ether-heptane (1:1) by slow evaporation. M.p. 165–166°C. ^{31}P NMR (CH_2Cl_2): 118.1. ^{19}F NMR($CDCl_3$): −74.73 (t, $^3J_{FCCH} = 8.6$ Hz). ^{1}H NMR($CDCl_3$): 1.37 (s, 6H, CMe_2), 1.53 (s, 6H, CMe_2), 1.72 (s, 12H, CMe_2), 3.84 (qd, $^3J_{FCCH} = 8.6$, $^3J_{POCH} = 5.2$ Hz, 2H, $POCH_2CF_3$), 6.95 (m, 4H, Ph), 7.12 (m, 6H, Ph), 7.19–7.33 (m, 10H, Ph), 7.51 (d, 2.3 Hz, 2H, aryl-H), 7.87 (d, 2.3 Hz, 2H, aryl-H). Anal. calcd. for $C_{50}H_{50}O_5F_3PS$: C, 70.57; H, 5.92. Found: C, 70.28; H, 6.05.

$O_2S[C_6H_2(CMe_2Ph)_2O]_2P(OCH_2CF_3)_3$ (2)

A solution of **1** (2.00 g, 2.35 mmol), trifluoroethanol (0.35 mL, 4.79 mmol), and N-chlorodiisopropylamine (0.35 mL, 2.38 mmol) in dichloromethane (50 mL) was stirred for 2 days. The solvent was removed; the residue was extracted with ether (75 mL) and filtered. The filtrate was concentrated to 20 mL, and hexane was added (80 mL). This solution on slow evaporation gave a yellow oil. The oil was recrystallized from boiling methanol (30 mL). When the solution came to about 20 mL, it formed a microcrystalline solid, which was separated by filtration, washed with methanol (5 mL), and air dried. Yield 1.3 g (53%). Single crystals suitable for an X-ray study were obtained from a solution of methanol-dichloromethane (1:1). Two types of crystals formed, one quickly that turned to powder on exposure to air (likely due to a loss of the solvent) and the other that formed that was stable to air. The stable crystal was used in the X-ray study. M.p. >143–145°C. ^{31}P NMR(CH_2Cl_2): −71.9, −85.5 (in a 2.8:1 ratio). ^{31}P NMR (toluene): −72.0, −85.1 (in a 5.7:1 ratio). ^{31}P NMR ($CDCl_3$: 295 K): −71.7, −85.6 (in a 3.2:1 ratio). ^{31}P NMR ($CDCl_3$: 220 K): −71.3, −86.2 (in a 4.2:1 ratio). ^{1}H NMR($CDCl_3$: 295 K): 1.36–1.69 (broad singlets, 30H, CMe_2), 3.16–4.30 (broad multiplets, 6H, $POCH_2CF_3$), 6.90–7.80 (broad singlets and multiplets, 24H, Ph/aryl-H). ^{1}H NMR($CDCl_3$: 220 K): 1.26–1.72 (broad singlets, 30H, CMe_2), 3.14–4.30 (broad multiplets, 6H, $POCH_2CF_3$), 6.84–7.80 (Doublets and multiplets, 24H, Ph/aryl-H). ^{19}F NMR($CDCl_3$): Isomer **A** (minor): −74.56 (t, $^3J_{FCCH} = 8.1$ Hz, 3F), −75.02 (t, $^3J_{FCCH} = 8.8$ Hz, 3F), −76.30 (t, $^3J_{FCCH} = 8.4$ Hz, 3F); Isomer **B** (major): −74.32 (t, $^3J_{FCCH} = 8.3$ Hz, 3F), −75.42 (br, 6F). Anal. calcd. for $C_{54}H_{54}O_7F_9PS$: C, 61.83; H, 5.19. Found: C, 61.68; H, 5.24.

$[SC_6H_2(CMe_2Ph)_2O]_2P(OCH_2CF_3)$ (3)

Diphenol **4** (6.3 g, 8.71 mmol) and phosphorus trichloride (0.80 mL, 9.17 mmol) were stirred in dichloromethane (120 mL). Triethylamine (2.50 mL, 18.0 mmol) was added dropwise over a period of 40 min, and the solution stirred further for 4 h. Triethylamine (1.30 mL, 9.34 mmol) and trifluoroethanol (0.70 mL, 9.57 mmol) were added, and the reaction mixture stirred for 24 h. The solvent was removed by distillation, and the residue was extracted with ether (150 mL) and filtered. Heptane (20 mL) was added and left under an argon flow. It formed a dark oil first, which was removed by decanting the solution. The mother liquor gave a crystalline solid, which was recrystallized once again from heptane-ether (10:50 mL). The crystalline solid was filtered, washed with heptane (2 × 10 mL), and dried. Yield 2.50 g (34%). Single crystals suitable for an X-ray study were obtained from ether-heptane (1:1) by slow evaporation. M.p. 149–151°C. ^{31}P NMR (CH_2Cl_2) : 18.1. ^{19}FNMR ($CDCl_3$) : −74.95 (t,$^3J_{FCCH}$ = 8.2Hz). ^{1}HNMR ($CDCl_3$): 1.51 (s, 6H, CMe_2), 1.59 (s, 6H, CMe_2), 1.66 (s, 12H, CMe_2), 2.67 (quintet, $^3J_{FCCH} = ^3J_{POCH}$ = 8.4 Hz, 2H, $POCH_2$ CF_3), 6.92 (br, 2H, aryl-H), 7.07–7.12 (m, 8H, aryl-H), 7.17–7.31 (m, 14H, aryl-H). Anal. calcd. for $C_{50}H_{50}O_3F_3PS_2$: C, 70.50; H, 5.92. Found: C, 70.43; H, 6.05.

$S_2[C_6H_2(CMe_2Ph)_2OH]_2$ (4) and $O_2S[C_6H_2(CMe_2Ph)_2OH]_2$ (5)

Sulfur dichloride (5.00 mL, 78.1 mmol) was added to a solution of bis(dimethylbenzyl)phenol (52.0 g, 157 mmol) in hexane (150 mL) and stirred. A catalytic amount of zinc chloride catalyst (50 mg) was added, and stirring continued for 2 days. The greenish solution was stirred with potassium bicarbonate (15 g) for 30 min, and the yellow solution filtered. The solvent was removed, and the oil was dissolved in hot acetic acid (50 mL) and left aside. It gave bright yellow crystals of the diphenol **4**, which was filtered, washed with acetic acid (2 × 10 mL), and air-dried for 2 weeks. Yield 6.7 g (5.9%). M.p. 150–155°C. ^{1}H NMR ($CDCl_3$): 1.57 (s, 12H, CMe_2), 1.64 (s, 12H, CMe_2), 5.92 (s, 2H, OH), 7.1–7.3 (m, 24H, Ph/aryl).

To the remaining acetic acid solution, additional acetic acid (70 mL) and hydrogen peroxide (30%, 30 mL) were added. The solution was heated for 2 h. The pasty mass was stirred with water (120 mL), and the solid filtered. The solid was dissolved in dichloromethane-heptane (125–50 mL), stirred with potassium bicarbonate and anhydrous magnesium sulfate for 10 min, and filtered. The filtrate on slow evaporation gave a crystalline solid of diphenol **5**. Yield 25.0 g (in two crops) (22%). M.p. 187–189°C. ^{1}H NMR ($CDCl_3$): 1.54 (s, 12H, CMe_2), 1.60 (s, 12H, CMe_2), 7.05 (m, 4H, Ph/aryl), 7.1–7.3 (m, 16H, Ph/aryl), 7.38 (m, 4H, Ph/aryl), 8.29 (s, 2H, OH). Anal. calcd. for $C_{48}H_{50}O_4S$: C, 79.74; H, 6.97. Found: C, 79.54; H, 6.97.

X-Ray Studies

The X-ray crystallographic studies were performed using a Nonius KappaCCD diffractometer and graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). Data were collected at 293 K, $\theta_{MoK\alpha} \leq 25°$. All of the data were included in the refinement. Structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least squares. Refinements were based on F^2 and computations were performed on a 2.6 GHz Pentium 4 computer using SHELXS-86 for a solution[9] and SHELXL-97 for refinement.[10] All of the nonhydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$.

RESULTS AND DISCUSSION

Crystallographic data are summarized in Table I. The atom-labeling schemes for **1–3** are given in the ORTEP plots of Figures 1–3, respectively. These figures were made using the ORTEP-III for Windows program.[11] Thermal ellipsoids are shown at the 50% probability level. Selected bond parameters are given in Tables II–IV.

TABLE I Crystallographic Data for Compounds 1–3

Compound	**1**	**2**	**3**
Formula	$C_{50}H_{50}F_3O_5PS$	$C_{54}H_{54}F_9O_7PS$	$C_{50}H_{50}F_3O_3PS_2$
Formula weight	850.93	1049.00	850.99
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Crystal size, mm	1.00 × 0.50 × 0.30	0.75 × 0.65 × 0.40	0.95 × 0.90 × 0.50
a (Å)	15.8463 (4)	13.2024 (2)	8.6698 (2)
b (Å)	16.9769 (4)	16.6343 (3)	11.4027 (3)
c (Å)	18.6606 (3)	24.1074 (3)	23.0933 (7)
α (°)	78.576 (1)	86.7769 (7)	84.806 (1)
β (°)	75.008 (1)	89.4847 (9)	86.872 (1)
γ (°)	71.039 (1)	89.1322 (8)	76.159 (2)
V (Å^3)	4550.3 (2)	5285.1 (1)	2206.3 (1)
Z	4	4	2
D_{calc} (g/cm^3)	1.242	1.318	1.281
$^{\mu}$MoKα (cm^{-1})	1.64	1.73	2.11
Total reflns	16007	18330	7664
Reflns with $I > 2\sigma_I$	10735	14212	6218
R^a	0.0506	0.1215	0.1209
R_w^b	0.1109	0.3446	0.3217

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

$^b R_w(F_o{}^2) = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4\}^{1/2}$.

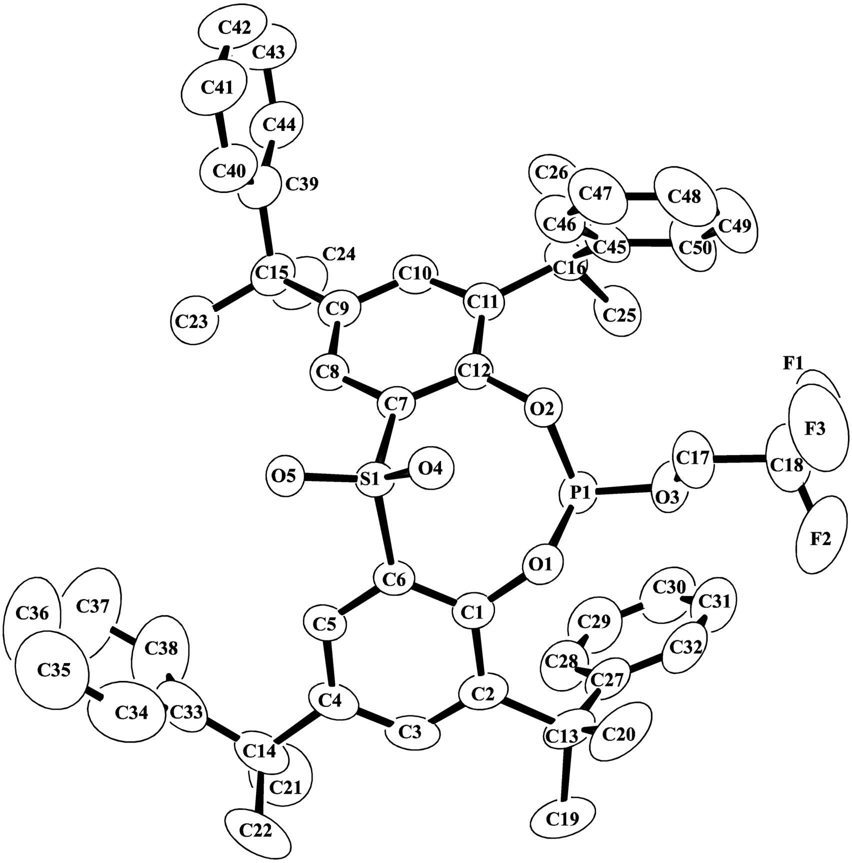


FIGURE 1 An ORTEP diagram of **1** (hydrogen atoms are omitted for clarity).

Syntheses

Two new diphenols were synthesized for use in this study. The thiodiphenol with very bulky groups could not be purified by crystallization and only produced a pasty mass. However, the minor impurity, dithio-diphenol **4**, crystallized readily from the paste when hot acetic acid was used as a solvent. The remaining paste was oxidized to sulfonyl-diphenol **5**, which was purified and easily crystallized. Phosphoranes similar to **2** were usually synthesized by reacting diphenols with tris(trifluoroethyl)phosphite.[5] However, such a reaction proceeded very slowly with this very bulky diphenol as tested in an NMR tube,

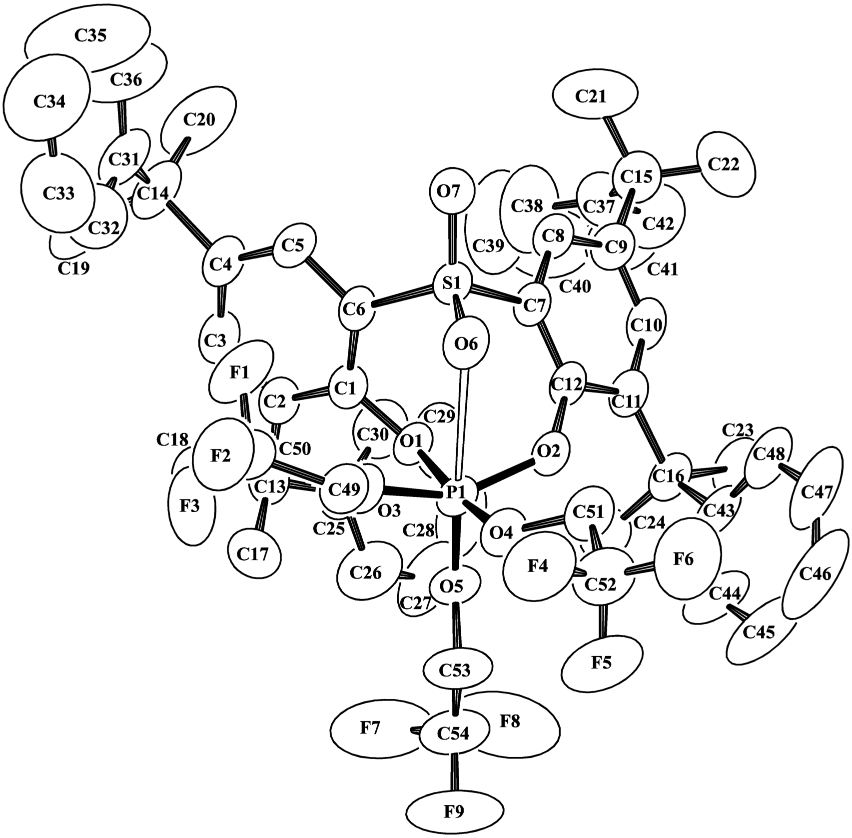


FIGURE 2 An ORTEP diagram of **2** (hydrogen atoms are omitted for clarity).

and the major products were phosphates. Hence, a different approach was employed. The phosphite starting material **1** was made first and then treated with two moles of trifluoroethanol in the presence of N-chlorodiisopropylamine in dichloromethane (Scheme 2). This method provided a higher yield and a lower amount of phosphates. The resulting phosphorane **2** proved to be very stable to moisture such that it could be crystallized under atmospheric conditions from methanol-dichloromethane or ethanol-chloroform. Only very slow hydrolysis was observed.

When this route was used to prepare a similar starting phosphite from the dithio-diphenol **4**, unexpectedly, phosphorane **3** was obtained as the final product (Scheme 3). This is possibly due to an intramolecular oxidation of phosphorus by the sulfur–sulfur bond. Though such an

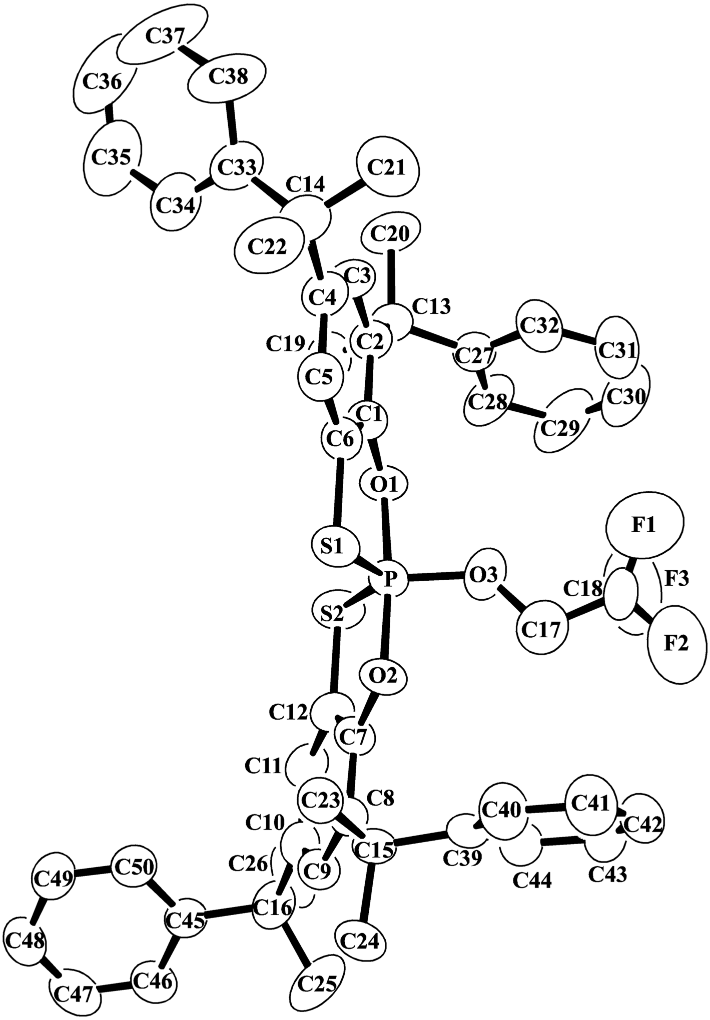
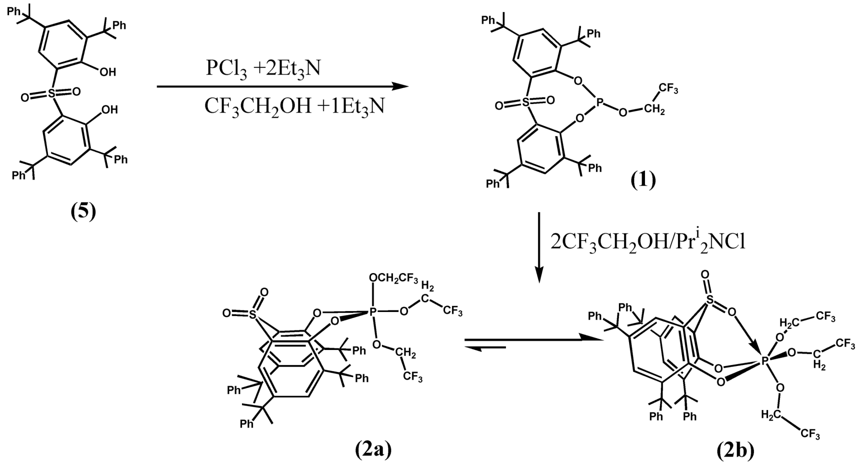


FIGURE 3 An ORTEP diagram of **3** (hydrogen atoms are omitted for clarity).

intramolecular oxidative addition is not known, an intermolecular oxidative addition of S—S bonds to phosphites yielding thiophosphoranes has been reported earlier.[12]

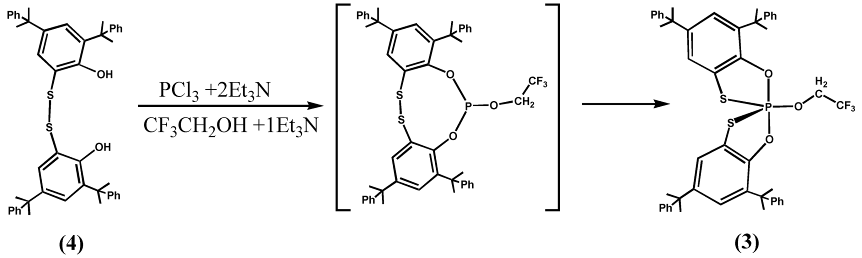
Structural Studies

Earlier studies have shown that sulfonyl group oxygen atoms can act as donors to the phosphorus atom depending on the steric bulk of the



(5) **(1)** **(2a)** **(2b)**

SCHEME 2

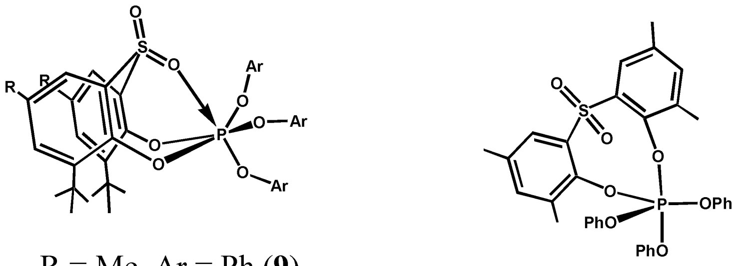


(4) **(3)**

SCHEME 3

eight-membered ring system and the electron-withdrawing ability of the other substituents present on the phosphorus atom.[5,6,13] For example, when there were no bulky groups, there was no donor interaction between oxygen and phosphorus as seen in the phosphorane **12** (Scheme 4).[6] In phosphorane **12**, the eight-membered ring has a twist-syn conformation with a P—O distance of 3.233(5) Å. When bulky groups were introduced closer to the phosphorus, as seen in phosphoranes **9** and **10**,[5] the eight-membered ring changed to a syn conformation and a moderate phosphorus–oxygen donor interaction was observed (with the P—O distances being 2.487(3) and 2.546(9) Å, respectively). When the electronegativity of the phosphorus substituents was increased using fluorine atoms, the interaction became very strong as seen in phosphorane **11**,[6] where the P—O distance was 1.936(7) Å.

When the bulky groups were retained and the electronegativity of the substituents was reduced by using alkyl groups, a very interesting



R = Me, Ar = Ph (**9**)
R = Bu^t, Ar = Ph (**10**)
R = Bu^t, Ar = C_6F_5 (**11**)

(**12**)

SCHEME 4

feature was observed. There were isomers at equilibrium with either a P—O interaction or no interaction, leading to the coexistence of penta- and hexa-coordinated phosphoranes in equilibrium (as shown in phosphoranes **6–8**, Scheme 5).[5,6] However, all three structures provided only the pentacoordinated phosphorus geometry with the ring occupying diequatorial positions with an *anti* conformation. The nature and strength of the other isomer remained unknown since it could not be obtained in a crystalline state.

TABLE II Selected Bond Lengths [Å] and Angles [deg] for 1

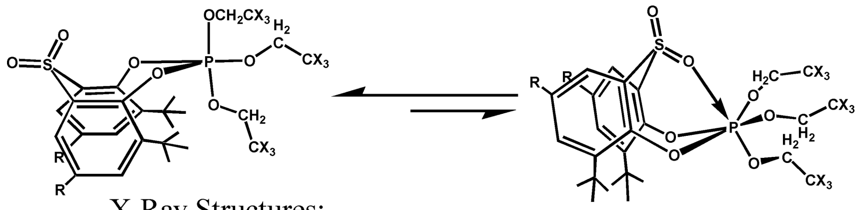
P(1)—O(1)	1.6463(18)	P(2)—O(6)	1.6476(17)
P(1)—O(2)	1.6489(16)	P(2)—O(7)	1.6468(17)
P(1)—O(3)	1.5972(19)	P(2)—O(8)	1.6021(18)
S(1)—O(4)	1.4293(16)	S(2)—O(9)	1.4324(18)
S(1)—O(5)	1.4354(17)	S(2)—O(10)	1.4323(18)
O(1)—P(1)—O(2)	100.80(9)	O(6)—P(2)—O(7)	101.83(8)
O(1)—P(1)—O(3)	97.45(10)	O(6)—P(2)—O(8)	94.70(9)
O(2)—P(1)—O(3)	96.15(9)	O(7)—P(2)—O(8)	95.33(9)
O(4)—S(1)—O(5)	118.27(10)	O(9)—S(2)—O(10)	118.60(11)
O(4)—S(1)—C(6)	109.51(10)	O(9)—S(2)—C(6A)	108.70(11)
O(5)—S(1)—C(6)	105.85(10)	O(9)—S(2)—C(7A)	109.49(11)
O(4)—S(1)—C(7)	109.53(10)	O(10)—S(2)—C(6A)	106.12(12)
O(5)—S(1)—C(7)	106.02(11)	O(10)—S(2)—C(7A)	105.46(10)
C(6)—S(1)—C(7)	107.07(10)	C(6A)—S(2)—C(7A)	108.01(11)
C(1)—O(1)—P(1)	121.74(15)	C(1A)—O(6)—P(2)	127.21(14)
C(12)—O(2)—P(1)	118.42(13)	C(12A)—O(7)—P(2)	125.63(15)
C(17)—O(3)—P(1)	125.17(17)	C(17A)—O(8)—P(2)	120.62(15)

TABLE III Selected Bond Lengths [Å] and Angles [deg] for 2

P(1)—O(1)	1.692(4)	P(2)—O(11)	1.684(4)
P(1)—O(2)	1.647(5)	P(2)—O(12)	1.641(4)
P(1)—O(3)	1.619(5)	P(2)—O(13)	1.614(4)
P(1)—O(4)	1.635(5)	P(2)—O(14)	1.642(4)
P(1)—O(5)	1.594(5)	P(2)—O(15)	1.599(5)
P(1)—O(6)	2.658(5)	P(2)—O(16)	2.753(5)
S(1)—O(6)	1.448(5)	S(2)—O(16)	1.450(5)
S(1)—O(7)	1.433(5)	S(2)—O(17)	1.434(5)
O(1)—P(1)—O(2)	88.4(2)	O(11)—P(2)—O(12)	88.9(2)
O(1)—P(1)—O(3)	87.9(2)	O(11)—P(2)—O(13)	87.3(2)
O(1)—P(1)—O(4)	170.1(3)	O(11)—P(2)—O(14)	171.2(2)
O(1)—P(1)—O(5)	92.1(2)	O(11)—P(2)—O(15)	91.5(2)
O(2)—P(1)—O(3)	149.9(3)	O(12)—P(2)—O(13)	146.7(2)
O(2)—P(1)—O(4)	88.5(2)	O(12)—P(2)—O(14)	89.1(2)
O(2)—P(1)—O(5)	104.1(3)	O(12)—P(2)—O(15)	105.5(2)
O(3)—P(1)—O(4)	90.1(2)	O(13)—P(2)—O(14)	89.7(2)
O(3)—P(1)—O(5)	105.9(3)	O(13)—P(2)—O(15)	107.7(3)
O(4)—P(1)—O(5)	97.8(3)	O(14)—P(2)—O(15)	97.3(2)
O(1)—P(1)—O(6)	88.9(2)	O(11)—P(2)—O(16)	87.9(2)
O(2)—P(1)—O(6)	74.6(2)	O(12)—P(2)—O(16)	73.1(2)
O(3)—P(1)—O(6)	75.5(2)	O(13)—P(2)—O(16)	73.7(2)
O(4)—P(1)—O(6)	81.2(2)	O(14)—P(2)—O(16)	83.3(2)
O(5)—P(1)—O(6)	178.3(2)	O(15)—P(2)—O(16)	178.4(2)
O(6)—S(1)—O(7)	117.3(3)	O(16)—S(2)—O(17)	116.4(3)
O(6)—S(1)—C(6)	110.6(3)	O(16)—S(2)—C(106)	110.1(3)
O(6)—S(1)—C(7)	107.8(3)	O(16)—S(2)—C(107)	107.4(3)
O(7)—S(1)—C(6)	108.2(3)	O(17)—S(2)—C(106)	108.3(3)
O(7)—S(1)—C(7)	108.6(3)	O(17)—S(2)—C(107)	108.1(3)
C(7)—S(1)—C(6)	103.4(3)	C(106)—S(2)—C(107)	106.1(3)
C(1)—O(1)—P(1)	127.6(4)	C(101)—O(11)—P(2)	128.1(4)
C(12)—O(2)—P(1)	130.6(4)	C(112)—O(12)—P(2)	131.6(4)
C(49)—O(3)—P(1)	127.8(4)	C(149)—O(13)—P(2)	126.1(4)
C(51)—O(4)—P(1)	130.1(5)	C(151)—O(14)—P(2)	129.4(4)
C(53)—O(5)—P(1)	124.1(5)	C(153)—O(15)—P(2)	124.1(5)
S(1)—O(6)—P(1)	101.9(2)	S(2)—O(16)—P(2)	99.8(2)

TABLE IV Selected Bond Lengths [Å] and Angles [deg] for 3

P—O(1)	1.694(5)	P—O(2)	1.711(5)
P—O(3)	1.595(6)	P—S(1)	2.078(3)
P—S(2)	2.085(3)		
O(1)—P—O(2)	174.2(3)	O(1)—P—O(3)	90.3(3)
O(2)—P—O(3)	95.5(3)	O(1)—P—S(1)	93.0(2)
O(2)—P—S(1)	85.2(2)	O(3)—P—S(1)	113.6(3)
O(1)—P—S(2)	84.9(2)	O(2)—P—S(2)	92.1(2)
O(3)—P—S(2)	114.5(3)	S(1)—P—S(2)	131.9(1)



X-Ray Structures:
R = Me, X= Cl (**6a**)
R = Me, X = F (**7a**)
R = Bu^t, X = F (**8a**)

(No structure;
only NMR data)
(**6b–8b**)

SCHEME 5

In the present study, with the use of bulky groups, the hexacoordinated isomer became easily stabilized and readily crystallized. This allowed us to study the structure of this missing component of the penta-hexa coordination equilibrium we reported earlier.[5,6] In solution, also, the hexacoordinated phosphorane was present in much higher proportion than in earlier cases where pentacoordinated forms remained as the major isomers.[5,6]

Table V summarizes the structural changes observed in these sulfonyl-containing phosphoranes. A gradual change from pentacoordination to hexacoordination is observed at phosphorus as one descends down the table.

The Mechanism of Hexacoordination

Generally, it is considered that pentacoordination to hexacoordination occurs through a Square Pyramidal (SP) geometry from a Trigonal Bipyramidal (TBP) geometry. A careful analysis of the coordination at these sulfonyl phosphoranes reveals that in addition to having a square pyramidal distortion on the pathway toward an octahedron, there is also a change in the ring orientation. Originally, when no coordination is present, the eight-membered ring occupies a diequatorial orientation, as seen in phosphoranes **6–8** (Scheme 5).[5,6] However, it changes to an axial-equatorial orientation before distorting toward the SP geometry. Such axial-equatorial orientation is seen in phosphorane **12**, where there is no bulky group.[6] However, when there are bulky groups, such axial-equatorial orientations are sterically less favored and bulky groups are even known to promote phenyl or ethyl groups to occupy axial positions.[14] However, in some cases, an axial-equatorial orientation is observed despite the presence of bulky groups.[15]

TABLE V The Tendency Toward Hexacoordination Influenced by Steric and Electronic Effects for a Series of Sulfonyl-Containing Phosphoranes

Phosphorane	*t*-Butyl groups	Trifluoroethoxy/ phenoxy	Donor interaction[a]	P—O distance, Å	TBP→SP %
12	No	Phenoxy	No (penta)	3.23	36[e]
6	Yes	Alkoxy	Equilibrium (penta)	—	—
7	Yes	Alkoxy	Equilibrium (penta)	—	—
8	Yes	Alkoxy	Equilibrium (penta)	—	—
2	Yes[b]	Alkoxy	Equilibrium (hexa)	2.75, 2.66	60 68
9	Yes	Phenoxy	Yes (hexa)	2.49	84
10	Yes	Phenoxy	Yes (hexa)	2.55	87
11	Yes	Phenoxy[c]	Yes (hexa)	1.94	91[e]
13[d]	Yes	Phenoxy[c]	Yes (pseudo-penta)	2.65	—

[a] Equilibrium denotes the existence of an isomeric penta-hexa coordination equilibrium in the solution. The solid state coordination at phosphorus is given in parentheses as found by X-ray analysis.

[b] Bulkier α,α-dimethylbenzyl group is used here.

[c] Highly electronegative pentafluorophenoxy groups are used for **11** and **13**.

[d] Phosphite **13** has P—O donor interaction[13] that is as strong as that found in phosphoranes.

[e] Compounds **11** and **12** deviate considerably from the Berry coordinate.

In Figure 6, it can be clearly seen that the eight-membered ring of **2** is in the pseudo axial-equatorial orientation of a distorted TBP geometry when the weaker P—O16 bond is not considered. It is possible that the diequatorial ring orientation hinders a distortion toward an SP and, hence, the coordination proceeds through the axial-equatorial ring orientational change. The SP distortion seems to be only partial, which allows one to easily see which ligands were in axial and equatorial groups in the original TBP intermediate. From the partial TBP orientation of **2** in Figure 6, it is apparent that the O11 and O14 are axially oriented, and O12, O13, and O15 are considered to occupy equatorial sites. The P—O11 bond is longer than the P—O12 bond by about 0.044(4) Å. In the pentacoordinated phosphorane **12** (Scheme 3), this difference was 0.065(4) Å.[6] Similarly, O13 and O15 have the shortest distances to the phosphorus. The O11-P-O14 angle of 171.2(2) and the O12-P-O13 angle of 146.7(2) show a slight movement toward the SP geometry, but it is very far from the SP geometry where these angles are expected to be similar. Thus, structural changes encountered for this series of sulfonyl-containing phosphoranes follow the mechanistic sequence TBP(ee) → TBP(ae) → [TBP(ae)-SP] → Octahedral.

NMR SPECTROSCOPY

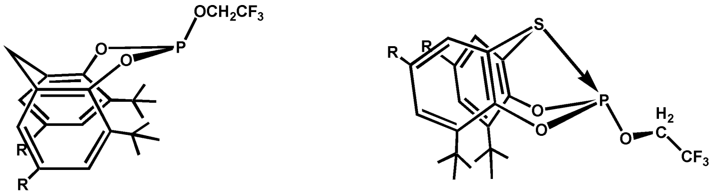
Isomerism and Fluxionality

As described before, there are two isomers present in solution for phosphorane **2**. The proton NMR was unresolvable even at −60°C, and, hence, it was not useful in making structural assignments. However, the fluorine NMR clearly shows that there are two isomers. The minor isomer has three sets of fluorine resonances of equal intensity, which suggests it to be the pentacoordinated form **2a**. The major isomer **2b** has two resonances in an intensity ratio of 1:2. The stronger resonance was very broad, suggesting an additional inequality or fluxionality possibly caused by the differences seen in Figure 6 and the rotation of the dimethylbenzyl groups. These differences are associated with the orientation of the three trifluoroethoxy groups. One is *trans* to the donor (attached to O15) and the other two are *cis* to the donor. Among the two *cis*-oriented groups, one is in a pseudo-axial site (attached to O14), and the other is located in a pseudo-equatorial site (attached to O13). They all can undergo exchange.

The phosphorus NMR for **2** readily shows two isomers as seen before in phosphoranes **6–8**.[5,6] However, as mentioned earlier, the hexacoordinated form is very predominant for **2**, whereas in **6–8**, the pentacoordinated form was predominant. The isomer ratio of **2** changed on cooling (3.2:1 at 295 K to 4.2:1 at 225 K) or on changing the solvent (2.8:1 in dichloromethane to 5.7:1 in toluene). This suggests that there is an active equilibrium for **2** in a solution similar to that observed for **6–8**.[5,6]

Chemical Shift Contradiction

Generally, when there is a donor interaction due to an increased electron density at phosphorus, an upfield chemical shift is expected and most often is observed. However, in this system of phosphoranes, **2** and **6–8**, the pentacoordinated forms have values of about −85 ppm, whereas the hexacoordinated forms have values of about −72 ppm. This contradiction is readily explained by the fact that the phosphorus resides in between two aromatic ring currents in the pentacoordinated form with a diequatorial orientation of substituents. This causes a shielding at phosphorus. Though a similar shielding effect has been understood in proton NMR,[1b,5,16] it has not been considered for other nuclei. In the hexacoordinated form, the phosphorus moves out of this shielding region. This leads to a loss of shielding and results in a downfield shift, and from this value, the coordination effect moves the chemical shift upfield. When the coordination is not too strong, the chemical shift we observe is still downfield to that of the pentacoordinated phosphorane. A similar downfield shift upon coordination can be seen in the earlier reported phosphite NMR values of **14**[16] and **15**[17] although they were not assigned these structures at that time (Scheme 6).



R = Bu^t, ^{31}P =125.9 (**14**) R = Bu^t, ^{31}P =143.0 (**15**)

SCHEME 6

The Structure of Phosphite 1

The phosphorus atom in phosphite **1** has the eight-membered ring in an *anti* conformation (Figure 4) and does not have any donor interaction. Although phosphorane **2** shows donor interaction (Figure 5) compared to the less bulky tert-butyl systems in **6–8**, phosphite **1** lacks this interaction despite the increased bulkiness of substituents. However, a phosphite with a less bulky tert-butyl system but with a stronger electron-withdrawing pentaflourophenoxy group[13] showed a fairly strong donor interaction that was nearly as strong as that of phosphorane systems **2** and **6–8**. This shows that there is an interplay of steric and electronic

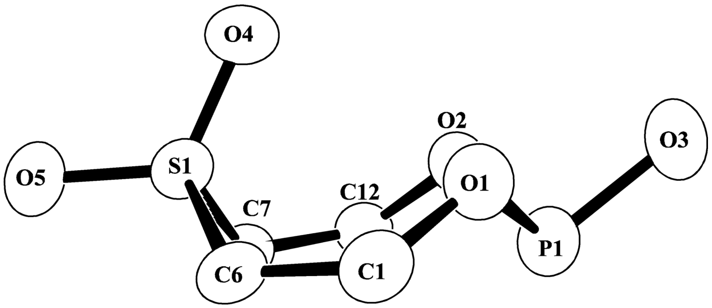


FIGURE 4 An ORTEP diagram of **1** showing the eight-membered ring conformation with the orientation of substituents at phosphorus and at the opposite sulfur atom.

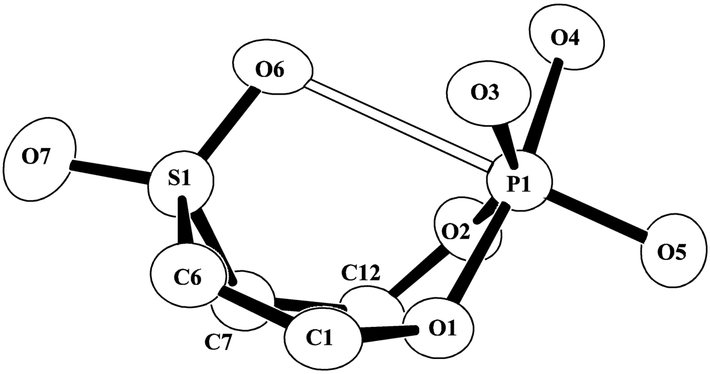


FIGURE 5 An ORTEP diagram of **2** showing the eight-membered ring conformation with the orientation of substituents at phosphorus and at the opposite sulfur atom.

factors in determining whether the donor interaction takes place or not.

The Structure and NMR of Phosphorane 3

X-ray analysis of phosphorane **3** (Figure 3) reveals that it has two thiocatechol-moieties with both sulfur atoms occupying equatorial positions. This leaves the bulky aryloxy groups in the axial positions and the

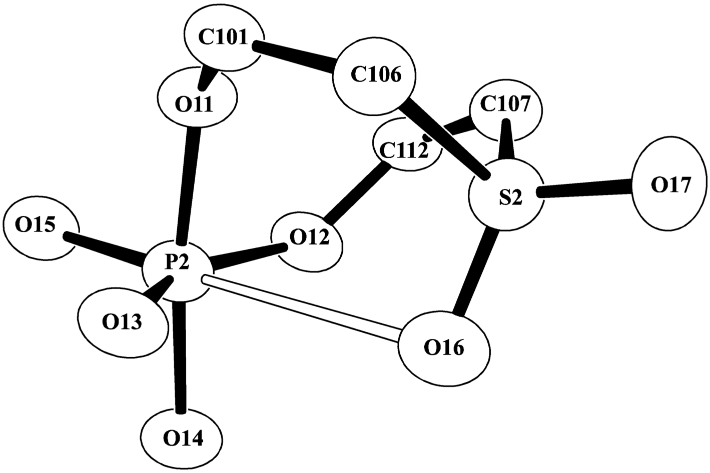


FIGURE 6 An ORTEP diagram of **2** (molecule 2) showing the pseudo axial-equatorial orientation of the eight-membered ring along with the substituents at phosphorus and at the opposite sulfur atom.

trifluoroethoxy group at an equatorial site. This is a unique occurrence in that no previous structure for any thiocatechol-based phosphorane is known in any form to compare with this structure. Earlier, we have observed that the bulky tert–butyl-containing aryloxy groups had the ability to stay in equatorial positions and allow phenyl or ethyl groups to reside at axial positions in systems with eight-membered rings.[14] However, in phosphorane **3**, less bulky sulfur atoms remain at the equatorial positions, and the more bulky dimethylbenzyl-containing aryloxy groups position themselves at the axial sites. NMR data does not show any fluxional behavior for **3** in contrast to that observed for phosphorane **2**.

The unusual positive value of ^{31}P NMR for phosphorane **3** is very much the same as found in other systems. Similar thiocatechol derivatives have been shown to have similar ^{31}P chemical shifts in the range of 16–19 ppm.[18] The trifluoroethoxy protons show a high degree of shielding of more than 1 ppm compared to phosphite **1**, most likely due to the aromatic ring currents of the dimethylbenzyl groups.

The Stability of Phosphoranes

Phosphorane **2** is very stable to moisture, similar to phosphoranes **6–8**. It was crystallized from alcohol under atmospheric conditions over a few weeks with very little decomposition. The extremely high stability provides insight into the pathways through which a possible hydrolysis/alcoholysis might occur. Such nucleophilic reactions can occur by a P—O bond cleavage through a dissociative pathway or by an associative pathway. If dissociation is the preferred pathway of hydrolysis, the introduction of bulky groups will destabilize and promote hydrolysis. However, if the associative pathway is the preferred route, then introducing bulky groups will stabilize and reduce or stop hydrolysis. So far, among all phosphoranes we have studied, phosphoranes with bulky groups are far more stable than those without bulky groups. If a dissociative pathway was operative, we would have seen only the hydrolyzed products for phosphorane **2** when kept in moist alcohols. The absence of such decay and unexpectedly high stability provides insight, suggesting that the preferred pathway is associative for hydrolysis/alcoholysis reactions of phosphoranes in this system.[2b,19]

REFERENCES

[1] (a) Pentacoordinated Molecules part 144; (b) For part 143, see N. V. Timosheva, A. Chandrasekaran, and R. R. Holmes, *Inorg. Chem.*, **45,** 3113 (2006).

[2] (a) R. R. Holmes, *Acc. Chem. Res.*, **37,** 746 (2004); (b) R. R. Holmes, *Acc. Chem. Res.*, **31,** 535 (1998).

[3] R. R. Holmes, *Phosphorus, Sulfur, and Silicon*, **180,** 1523 (2005).

[4] N. V. Timosheva, A. Chandrasekaran, R. O. Day, and R. R. Holmes, *J. Am. Chem. Soc.*, **124,** 7035 (2002).

[5] A. Chandrasekaran, R. O. Day, and R. R. Holmes, *J. Am. Chem. Soc.*, **119,** 11434 (1997).

[6] A. Chandrasekaran, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **36,** 2578 (1997).

[7] (a) R. Bishop, *Org. Synth. Coll. Vol.*, **9,** 692 (1998); (b) *Org. Synth.*, **70,** 120 (1992); (c) G. Brauer, Ed., *Handbook of Preparative Inorganic Chemistry* (2nd ed.), Vol. 1, pp. 370–371. (Academic Press, New York, 1963).

[8] (a) J. A. Riddick and W. B. Bunger, *Organic Solvents: Physical Properties and Methods of Purification*, 3rd ed., *Techniques of Chemistry* series, Volume II, Chapter V, 572–877, Wiley Interscience, New York, 1970; (b) A. I. Vogel, *Textbook of Practical Organic Chemistry* (Longman, London, 1978).

[9] G. M. Sheldrick, *Acta Crystallogr.*, **A46,** 467 (1990).

[10] G. M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement, University of Gottingen, Gottingen, Germany, 1997.

[11] L. J. Farrugia, *J. Appl. Cryst.*, **30,** 565 (1997).

[12] (a) D. B. Denney, D. Z. Denney, and L. T. Liu, *Phosphorus, Sulfur, Relat. Elem.*, **22,** 71 (1984); (b) D. B. Denney, D. Z. Denney, P. J. Hammond, C. Huang, L. T. Liu, and K. S. Tseng, *Phosphorus, Sulfur Relat. Elem.*, **15,** 281 (1983); (c) Y. Kimura, T. Kokura, and T. Saegusa, *J. Org. Chem.*, **48,** 3815 (1983).

[13] P. Sood, A. Chandrasekaran, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **37,** 6329 (1998).

[14] (a) N. V. Timosheva, A. Chandrasekaran, T. K. Prakasha, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **35,** 6552 (1996); (b) N. V. Timosheva, T. K. Prakasha, A. Chandrasekaran, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **34,** 4525 (1995).

[15] (a) P. Kommana, N. S. Kumar, (b) J. J. Vittal, E. G. Jayasree, E. D. Jemmis, and K. C. K. Swamy, *Organic Lett.*, **6,** 145 (2004); (b) M. A. Said, M. Pulm, R. H. Irmer, and K. C. K. Swamy, *Inorg. Chem.*, **36,** 2044 (1997).

[16] W. M. Abdou, D. B. Denney, D. Z. Denney, and S. D. Pastor, *Phosphorus, Sulfur, Relat. Elem.*, **22,** 99 (1985).

[17] T. K. Prakasha, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **31,** 3391 (1992).

[18] D. Stollberg, J. Gloede, and K. Andra, *Z. Anorg. Allg. Chem.*, **527,** 180 (1985).

[19] (a) A. Chandrasekaran, P. Sood, and R. R. Holmes, *Inorg. Chem.*, **37**, 459 (1998); (b) Many associative mechanisms are supported for phosphorus reactions proceeding through pentacoordinated excited states, see R. R. Holmes, *Pentacoordinated Phosphorus—Reaction Mechanisms*, Vol. II, ACS Monograph 176 (American Chemical Society, Washington, D.C., 1980); (c) Structural aspects of these classes of compounds are summarized in the following: R. R. Holmes, *Pentacoordinated Phosphorus—Structure and Spectroscopy*, Volume I, ACS Monograph 175 (American Chemical Society, Washington, D.C., 1980).