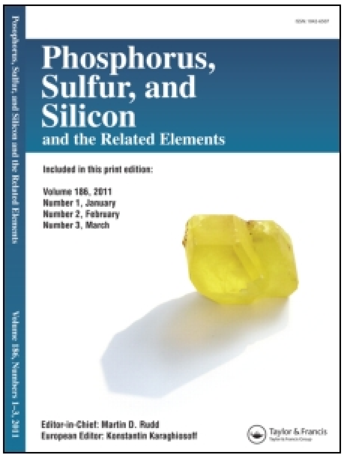

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A STABLE SPIROCYCLIC TETRAOXA(HYDRO)-PHOSPHORANE CONTAINING A SIX-MEMBERED RING

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The tetraoxa(hydro) spirophosphorane, **3** containing a six and five-membered ring is isolated in 66% yield from the reaction of 2-chloro-1,3,2-dioxaphosphorinane, **1** and triethylammonium perfluoropinacolate, **2**. Hexaflouroacetone inserts into the P—H bond of **3** to form the pentaoxaphosphorane, **6** which is obtained in a different way from phosphite, **5** and hexafluoroacetone. 2-Methoxy-1,3,2-dioxaphosphorinane, **7** and hexafluoroacetone furnish spirophosphorane, **8**, the methoxy derivative of **3**. ^1H and ^{19}F NMR spectra of the phosphoranes show rapid pseudorotation processes equilibrating substituent positions in the trigonal bipyramidal geometry at phosphorus. The ^1H NMR data of the six-membered ring are in accord with a time averaged conformation of a flattened chair.

INTRODUCTION

Many tetraoxa(hydro) spirophosphoranes containing two five-membered rings show tautomeric equilibria in solution between a tri- and penta-coordinated form depending on steric and electronic factors, temperature and basicity of the solvent.[1-5] Only very few can be converted into the corresponding stable phosphoranide.[6,7] A tetraoxa(hydro) spirophosphorane with a five- and six-membered ring at phosphorus could not be isolated yet.[8,9] Since the $OC(CF_3)_2C(CF_3)_2O$ grouping stabilizes halo, hydro, amino and hydroxyphosphoranes[10] the hydrophosphorane in question should be isolable taking advantage of this electron withdrawing and bulky bidentate substituent.

RESULTS AND DISCUSSION

Using a modified literature method,[11] 2-chloro-1,3,2-dioxaphosphorinane[12,13] **1** and triethylammonium perfluoropinacolate[14] **2** reacted to give the tetraoxa(hydro) phosphorane **3** in 66% yield (eq. 1), a colourless liquid (b.p. 68°C/0.01 Torr). Hexafluoroacetone easily inserted into the P—H bond of **3** with formation of the pentaoxaphosphorane **6** (eq. 4), a colourless solid (m.p. 102°C) which was formed also in oxidative addition of hexafluoroacetone to the phosphorinane **5** (eq. 3).

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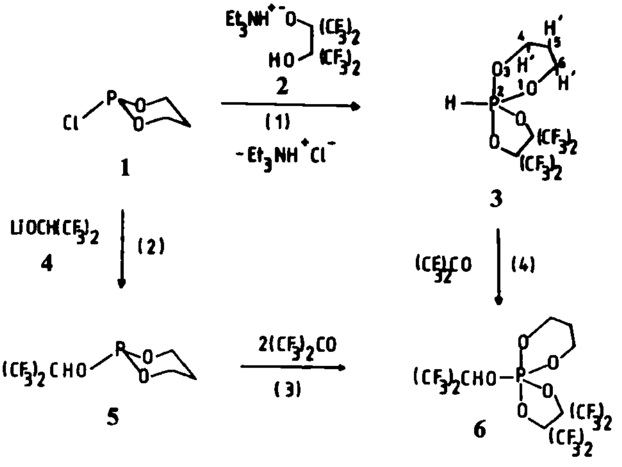
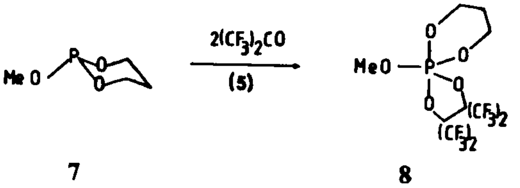
Compound **5** was obtained from the nucleophilic displacement reaction of **1** and the lithium derivative[15] **4** of hexafluoroisopropanol (eq. 2). 2-Methoxy-1,3,2-dioxaphosphorinane[16] **7** reacted with hexafluoroacetone yielding the pentaoxa spirophosphorane **8** (eq. 5), which is a colourless solid (m.p. 45°C). Compound **8** is considered the methoxy derivative of **3**.

The mass spectra of **3**, **5**, **6** and **8** exhibit the fragments M^+, M^+—H(**3**), M^+—F (**6** and **8**), M^+—CH_2O (**3**, **6** and **8**), M^+—C_3H_5O (**3**, **5**, **6** and **8**), M^+—CF_3 (**3**, **6** and **8**), M^+—$OCH(CF_3)_2$ (**5** and **6**) and CF_3^+ (**3** and **6**). Ions of highest abundance are M^+—CH_2O (**3**), M^+—$OCH(CF_3)_2$ (**5**), CF_3^+ (**6**) and M^+—C_3H_5O (**8**).



SCHEME 1



SCHEME 2

The P—H stretching frequency is observed in the IR spectrum of **3** at 2446 cm^{-1} proving that hydrogen is bound in the equatorial position of a trigonal bipyramid.[17] The valence modes for C—H and C—F are found in the range of 2970–2895 cm^{-1} and 1350–1100 cm^{-1}, respectively.

The ^1H, ^{19}F and ^{31}P NMR data of **3**, **6** and **8** are listed in Table I. The ^{31}P shift values are characteristic of compounds with penta-coordinate phosphorus (for the ^{31}P and $^{31}P\{^1H\}$ spectrum see Figure 1). Only one signal for the ring-CF_3 groups is observed in the ^{19}F NMR spectra of **3**, **6** and **8**, indicating rapid substituent permutation in the trigonal bipyramidal structure at phosphorus. The magnetic non-equivalences (MNE) between H and H′ (compiled in Table II) are relatively small compared with dioxaphosphorinanes containing three-coordinate phosporus.[12]

TABLE I

Chemical shift values δ (ppm, in frames) and coupling constants (in Hz) of **3**[a] (upper entry), **6**[b] (middle entry), and **8**[c] (lower entry) in $CDCl_3$. Coupling constants are found in the column under the signal, where they have been observed. Bracketed values for **8** were obtained by first order analysis of its deceptively simple spectrum and have to be regarded as line positions, not as coupling constants.

	P	4-H	4-H′	5-H	5-H′	6-H	6H′
P	− 35.75 − 50.80 − 47.95	17.3	17.3	0.7	1.1	17.3	17.3
4-H	15.2 17.1 17.2	4.203 4.569 4.250	− 12.0 − 11.5	9.5 10.5 (7.1)	6.2 5.6 (6.0)	1.8 1.4	− 1.2 − 0.8
4-H′	15.2 17.1 17.2	− 12.0 − 11.5	4.209 4.600 4.050	7.1 6.8 (7.1)	2.7 3.3 (6.0)	− 1.2 − 0.8	1.6 1.4
5-H		9.5 10.5 (6.9)	7.1 6.8 (6.9)	2.239 2.497 2.036	− 14.5 − 14.6 − 14.2	9.5 10.5 (6.9)	7.1 6.8 (6.9)
5-H′	2.3 1.5	6.2 5.6 (6.3)	2.7 3.3 (6.3)	− 14.5 − 14.6 − 14.2	1.933 2.266 1.970	6.2 5.6 (6.3)	2.7 3.3 (6.3)
6-H	15.2 17.1 17.2	1.8 1.4	− 1.2 − 0.8	9.5 10.5 (7.1)	6.2 5.6 (6.0)	4.203 4.569 4.050	
6-H′	15.2 17.1 17.2	− 1.2 − 0.8	1.6 1.4	7.1 6.8 (7.1)	2.7 3.3 (6.0)	− 12.0 − 11.5	4.209 4.600 4.050

[a] $\delta_H(PH) = 7.29$ ($^1J_{PH} = 925.3$, $^5J_{HH} = 0.5$, $^5J_{HH'} = 0.6$ Hz); $\delta_{FH'}(\text{ring-}CF_3) = 69.74$ ($^4J_{PF} = 2.4$ Hz).

[b] $\delta_H[OCH(CF_3)_2] = 5.413$ ($^3J_{PH} = 13.8$, $^3J_{FH} = 5.8$ Hz); $\delta_F[OCH(CF_3)_2] = -74.91$, $\delta_F(\text{ring-}CF_3) = -68.91$.

[c] $\delta_H(OMe) = 3.780$ ($^3J_{PH} = 14.0$ Hz); $\delta_F(\text{ring-}CF_3) = -74.29$.

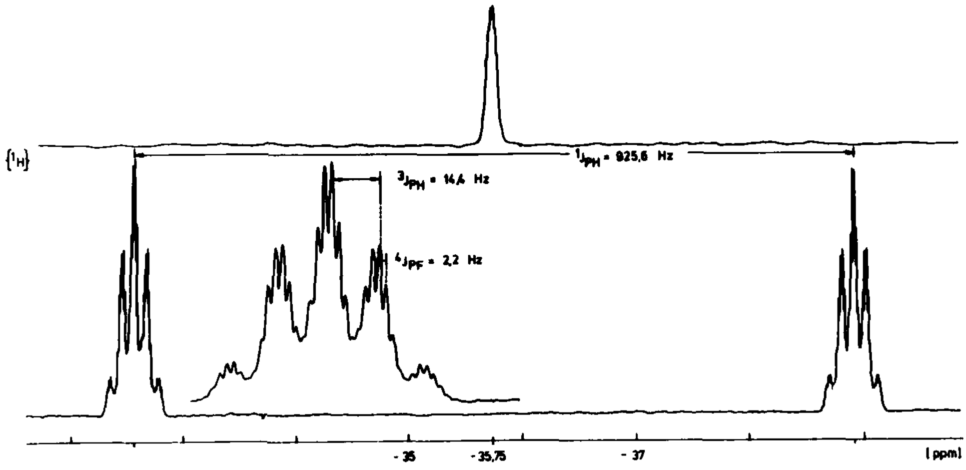


FIGURE 1 ^{31}P NMR spectrum of **3** at 145.72 MHz.

TABLE II

Magnetic non-equivalences (MNE) ν_H-$\nu_{H'}$ between axial and equatorial protons (in Hz)

	5-H	4,6-H
3	110.3	2.5
6	83.2	−11.3
8	23.8	0

These findings imply a time-averaged geometry at phosphorus with the oxygen atoms in the phospholane ring and the exocyclic substituent exchanging their positions occurring fast, versus the six-membered ring. A Karplus type analysis of the proton-proton coupling constants indicates that the dioxaphosphorinane ring is a distinctly flattened chair, where the difference in shift values of the geminal protons is smaller than in the nearly ideal chairs[12] (Figure 2).

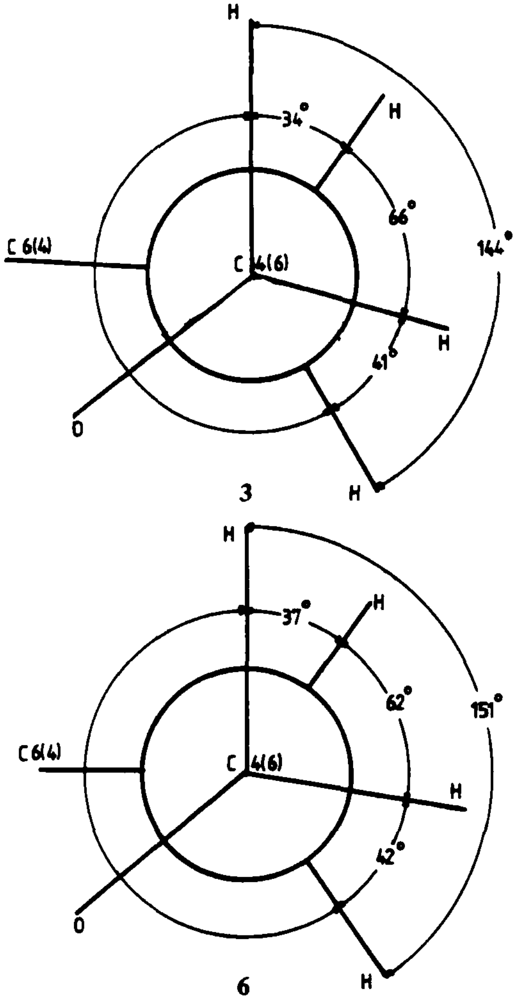


FIGURE 2 Dihedral angles along C4—C5 and C5—C6 in **3** and **6** (see text).

EXPERIMENTAL

The appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work. IR spectra were obtained on a Perkin Elmer 577 instrument, mass spectra on a Varian-MAT CH 7 spectrometer. NMR spectra were recorded on a Bruker WH 360 instrument at 360.08 MHz (^{1}H, internal TMS), 338.68 MHz (^{19}F, external CCl_3F) and 145.72 MHz (^{31}P, external 85% H_3PO_4). Chemical shifts were reported as downfield positive. Measurements were conducted on $CDCl_3$ solutions (ca. 10%, V/V).

Compounds **1**, **2**, **4** and **7** were synthesized according to literature procedures[12-16].

4,4,5,5-Tetrakis(trifluoromethyl)-spiro[1,3,2λ^5-dioxaphospholane-2,2'-[1,2,3λ^5]-dioxaphosphorinane] (**3**). Compound **2** (13.00 g, 30 mmole) in 100 ml diethylether and 4.25 g (30 mmole) of **1** were combined at −30°C. After stirring for 1 hr at −30°C the reaction mixture was allowed to warm up to room temperature. Triethylammonium chloride was removed by filtration and the solvent was distilled off. The remaining liquid was distilled at 68°C/0.01 Torr. The yield was 9.69 g (74%) of **3**.

IR(liquid): 2966 st, 2905 st(ν_{CH}); 2446 st(ν_{PH}); 1350 − 1100 sst (ν_{CF}). MS(25 eV, 25°C): m/e: 438(M^+, 4%), 437(M^+—H, 20), 409(M^+—CHO, 9), 408(M^+—CH_2O, 100), 381(M^+—C_3H_5O, 83), 380(M^+—C_3H_6O, 30), 369(M^+—CF_3, 80), 69 (CF_3^+, 5), 59($C_3H_5O^+$, 17), 58(C_3H_4O, 73), and other fragments. $C_9H_7F_{12}P$ (438.12): Calcd.: C, 24.67; H, 1.61; F, 52.04. Found: C, 24.51; H, 1.51; F 52.10.

2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]-1,3,2-dioxaphospholane (**5**). Compound **4** (7.26 g, 42 mmole) and 5.16 g (37 mmole) of **1** were allowed to react for 3 hr at room temperature. After vacuum distillation at 81°C/20 Torr 7.54 g of **5** (76%) were obtained.

MS(70 eV, 20°C) :m/e: 272(M^+, 12%), 217(M^+—C_3H_3O, 5), 215(M^+—C_3H_5O, 8), 214(M^+—C_3H_6O, 2), 166($(CF_3)_x2CHO^+$, 10), 132($C_3HF_5^+$, 20), 129($C_3HF_4O^+$, 16), 121($C_3H_6O_3P^+$, 20), 113($C_3HF_4^+$, 18), 105(M^+—$C_3HF_6O^+$, 18), 99($C_2H_2F_3O^+$, 21), and other fragments. NMR: ^{1}H: $\delta = 1.63$(5-H(eq), $^3J_{H(ax)H} = 2.20$, $^3J_{H(eq)H} = 2.20$, $^2J_{H(ax)H} = 14.50$, $^4J_{PH} = 2.20$ Hz), 2.49(5-H(ax), $^3J_{H(ax)H} = 12.80$, $^3J_{H(eq)H} = 4.60$ Hz), 3.98(6,4-H(eq), $^2J_{H(ax)H} = 16.20$, $^3J_{PH} = 10.60$ Hz), 4.51(6,4 H(ax), $^3J_{H(ax)H} = 12.80$, $^3J_{PH} = 3.20$ Hz), 4.62($HC(CF_3)_2$, $^3J_{PH} = 8.00$, $^3J_{FH} = 6.00$ Hz); ^{19}F: $\delta = -76.90$; ^{31}P: $\delta = 133.9$. $C_6H_7F_6O_3P$ (272.13): Calcd.: C, 26.49; H, 2.59. Found: C, 26.23; H, 2.62.

4,4,5,5-Tetrakis(trifluoromethyl)-2-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]spiro[1,3,2λ^5-dioxaphospholane-2,2' -[1,3,2λ^5] dioxaphosphorinane] (**6**). Compound **5** (3.71 g, 13.6 mmole) and 10.00 g (60 mmole) of hexafluoroacetone were allowed to react for 10 hrs at room temperature. After removing excess hexafluoroacetone 8.05 g(98%) of **6** (m.p. 102°C) were obtained.

MS(70eV, 30°C): m/e: 604(M^+, 11%), 585(M^+—F, 12), 574(M^+—CH_2O,9), 547(M^+—C_3H_5O, 65), 535(M^+—CF_3, 36), 438(M^+—C_3F_6O, 52), 437(M^+—C_3HF_6O, 6), 398($C_6H_3O_4F_{12}P^+$, 76) 378($C_6H_2O_4F_{11}P^+$, 19), 151($C_3HF_6^+$, 38), 69(CF_3^+, 100), 57 ($C_3H_5O^+$, 45), and other fragments. $C_{12}H_7F_{18}O_5P$ (604.08: Calcd.: C, 23.86; H, 1.17; F, 56.61. Found: C, 23.71; H, 1.28; F, 56.80.

4.38 g (10 mmole) of Compound **3** and 3.32 g (20 mmole) of hexafluoroacetone were allowed to react for 24 hrs at 60°C. After removal of volatiles 5.80 g (96%) of **6** were obtained.

2-Methoxy-4,4,5,5-tetrakis(trifluoromethyl)-spiro-[1,3,2λ^5-dioxaphospholane-2,2'[1,3,2λ^5]-dioxaphosphorinane] (**8**). Compound **7**(6.50 g, 48 mmole) and (96 mmole) of hexafluoroacetone were allowed to react for 24 hrs at room temperature. After pumping off volatiles and recrystalization of the remaining solid from 50 ml pentane 22.50 g (92%) of **8** were obtained (m.p. 45°C).

MS(30 eV, 30°C): m/e: 468(M^+, 0.1%), 449(M^+—F, 4), 438(M^+—CH_2O, 21), 412(M^+—C_3H_4O, 9), 411(M^+—C_3H_5O, 100), 399(M^+—CF_3, 33), 302(M^+—C_3F_6O, 3), 57($C_3H_5O^+$, 5), and other fragments. $C_{10}H_9F_{12}O_5P$ (468.13): Calcd.: C, 25.66; H, 1.94; F, 48.70. Found: C, 25.81 H, 1.97; F, 48.30.

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