Cyclisation reactions with hexafluoroacetone and phosphonous acid derivatives containing the trifluoromethyl and pentafluoropropenyl group; molecular structures of two 1,3,2$\lambda^5\sigma^5$-dioxaphospholanes†

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Abstract

1,3,2$\lambda^5\sigma^5$-Dioxaphospholanes have been obtained from trifluoromethylphosphonous acid diethyl ester, the corresponding bis(diethyldiamide), (*Z*)-1,2,3,3,3-pentafluoropropenylphosphonous acid diethyl ester and hexafluoroacetone. (*Z*)-1,2,3,3,3-Pentafluoropropenylphosphonous acid bis(diethylamide) furnished, unexpectedly, 2-bis(diethylamino)-2,3-difluoro-4,5,5-tris(trifluoromethyl)-1,2$\lambda^5\sigma^5$-oxaphospholene-(3). The structures of the two CF_3 group-containing dioxaphospholanes were confirmed by single-crystal X-ray investigations and shown to exhibit distorted trigonal bipyramids with CF_3 occupying the axial position.

Introduction

The oxidative addition of hexafluoroacetone to $\lambda^3\sigma^3$P species containing perfluoroalkyl or perfluoroalkenyl groups has been previously investigated in the case of (*Z*)-$CF_3CF{=}CFPMe_2$ only, where a 1,2$\lambda^5\sigma^5$-oxaphosphetane was obtained [1]. Here we describe reactions with the phosphonous acid derivatives $CF_3P(OEt)_2$ (**1a**) [2], $CF_3P(NEt_2)_2$ (**1b**) [3], (*Z*)-$CF_3CF{=}CFP(NEt_2)_2$ (**3b**) [4] and (*Z*)-$CF_3CF{=}CFP(OEt)_2$ (**3a**) [4]. The pentafluoroalkenyl moiety offers additional reactive sites like the isocyanato or vinyl grouping in $(RO)_2PNCO$ or $Ph_2PCH{=}CH_2$ [5].

Results and discussion

The trifluoromethylphosphonous acid derivatives **1a** or **1b** and hexafluoroacetone reacted to give the $\lambda^5\sigma^5$-dioxaphospholanes **2a** and **2b** in a

†Dedicated to Professor Alois Haas on the occasion of his 60th birthday.

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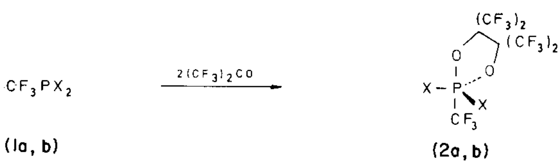
1:2 ratio [6] as low-melting colourless, moisture-sensitive solids (see Scheme 1).

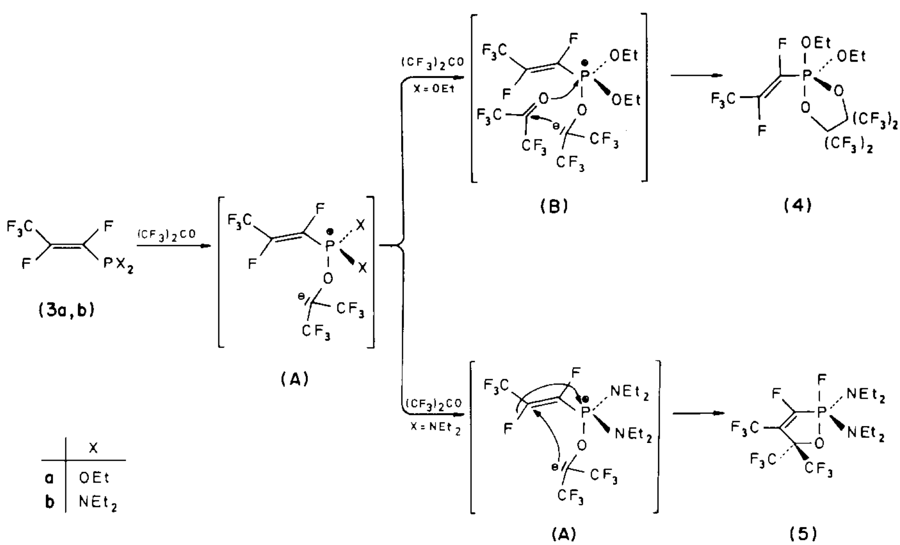
In the case of (*Z*)-1,2,3,3,3-pentafluoropropenylphosphonous acid diethylester (**3a**), a liquid dioxaphospholane **4** was obtained. However, the diamide **3b** added hexafluoroacetone in a rather surprising manner which had previously not been observed to furnish the $\lambda^5\sigma^5$-oxaphospholene-(3) (**5**) in 1:1 stochiometry (see Scheme 2). The fluorophosphorane **5** was formed probably from intermediate A via the nucleophilic attack of the carbanion and a 1,3-fluoride shift, whereas 1:2 addition (B) was preferred in the case of **3a**.

^{31}P NMR data unequivocally indicate the pentacoordinate character of phosphorus (see Table 1). The small $^2J_{PF}$ values for **2a** and **2b** (108.8 and 79.0 Hz) show that, despite rapid pseudorotation, rotamers with CF_3 in the axial position are apparently well populated ($^2J_{PF} = 150$ Hz for $CF_3PF_2(NMe_2)_2$



	X
a	OEt
b	NEt$_2$

Scheme 1.



	X
a	OEt
b	NEt$_2$

Scheme 2.

TABLE 1

^1H, ^{19}F and ^{31}P NMR data for **2a**, **2b**, **4** and **5** (J values given in Hz)

Compound	^1H chemical shifts[a] (ppm)		^{19}F chemical shifts[a] (ppm)					^{31}P chemical shifts[a] (ppm)
	CH_3 ($^3J_{HH}$)	CH_2 ($^3J_{PH}$)	(P)CF_3 ($^2J_{PF}$)	$OC(CF_3)_2$	$CF_3{}^3$ ($^4J_{F1F3}$), $^4J_{PF3}$)	F^1 ($^2J_{PF1}$)	F^2 ($^3J_{PF2}$)	
2a	1.21 (7.2)	2.98 (4.8)	−77.9 (108.8)	−72.5				−57.8
2b	1.10 (7.1)	3.0–3.4[b]	−62.0 (79.0)	−72.1				−29.3
4	1.20 (7.0)	4.0–4.4[b]		−72.8[c]	−71.9[d] 9.2, 0.9)	−149.3[e] (77.9)	−164.5 (13.8)	−53.4
5[f]	1.00 (7.0)	2.5–3.6[b]		−77.3[g]	−62.8 (18.8, 1.7)	−100.1 (90.6)	–	−57.8

[a]Highfield shifts allocated negative signs (TMS, CCl_3F and 85% H_3PO_4 used as standards).
[b]ABM_3X system.
[c] $^4J_{PF} = 1.0$ Hz.
[d] $^3J_{F2F3} = 22.5$ Hz.
[e] $^3J_{F2F1} = 144.9$ Hz.
[f]$\delta_F = -57.5$ ($^1J_{PF} = 747.0$, $^3J_{FF1} = 10.5$ Hz) ppm.
[g] $^5J_{F1F4} = 1.2$ Hz.

with CF_3 equatorially bonded [7]). Since no X-ray data are available for **4** one could postulate the equatorial position of the $CF_3CF{=}CF$ group in the ground state only from the direct P–C coupling constant $^1J_{PC1} = 285.0$ Hz. The steric requirements for this substituent may not favour the axial site (see Table 2) [8].

TABLE 2

^{13}C NMR data for compounds **4** and **5** [lowfield shifts (standard TMS) allocated positive signs; J values given in Hz]

Compound	^{13}C chemical shifts (ppm)				
	C^1 ($^1J_{CF1}$, $^1J_{PC1}$)	C^2 ($^2J_{CF1}$, $^2J_{CF3}$)	C^3 ($^1J_{CF3}$)	C^4 ($^1J_{CF}$)	C^5
4[a]	156.9[b] (295.0, 285.0)	119.5[c] (38.1, 16.7)	121.8 (293.0)	120.7[d] (293.0)	82.0
5[e]	169.9[f] (332.0, 263.0)	114.5[g] (49.2, 36.9)	120.5[h] (275.0)	121.5[i] (290.0)	78.4[j]

[a] $\delta = 66.5$ (CH_2); 10.5 (CH_3) ppm.
[b] $^2J_{CF2} = 44.0$ Hz.
[c] $^1J_{CF2} = 274.0$ Hz.
[d] $^3J_{CP} = 7.8$ Hz.
[e] $\delta = 43.0$ (CH_2); 14.0 (CH_3) ppm.
[f] $^2J_{CF} = 64.0$ Hz.
[g] $^3J_{C(P)F} = 9.8$, $^2J_{CP} = 7.4$ Hz.
[h] $J_{CF1} = 22.6$, $^4J_{C(P)F} = 2.5$, $^3J_{CP} = 2.5$.
[i] $^4J_{CF3} = 2.5$ Hz.
[j] $^2J_{CF} = 33.0$, $^2J_{CP} = 6.5$ Hz.

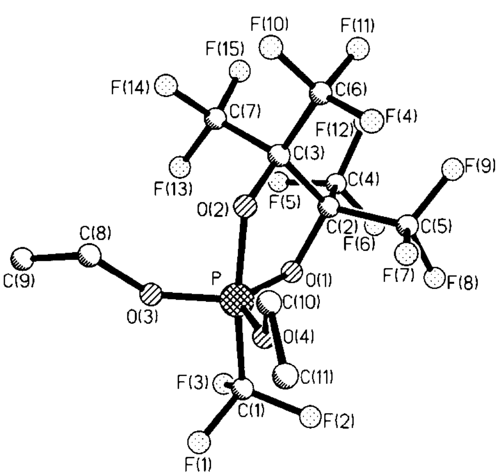


Fig. 1. View of the molecular structure of **2a** (hydrogen atoms omitted for clarity).

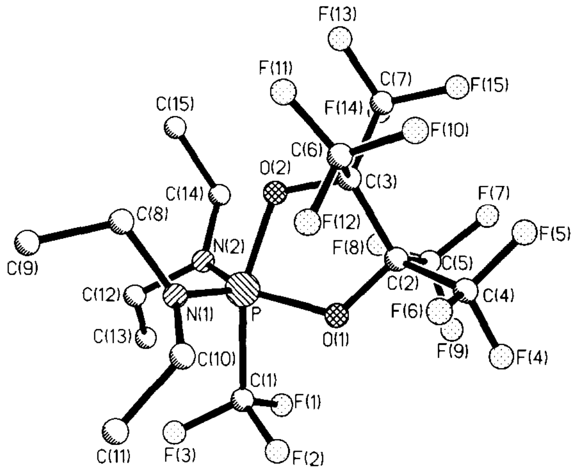


Fig. 2. View of the molecular structure of **2b** (hydrogen atoms omitted for clarity).

From single-crystal X-ray studies for both molecules **2a** and **2b** (Figs. 1 and 2), the pentacoordinated phosphorus is found to lie in the centre of a trigonal bipyramid (tbp) with one oxygen atom, O(2), of the five-membered ring in an apical and the other, O(1), in an equatorial position. The second apical site is occupied by C(1). In **2a**, the bond angles at phosphorus show significant distortion from the ideal tbp: the angle O(1)–P–R(2) (**2a**: R = O(3, 4); **2b**: R = N(1,2)) is widened by 12.0(2)°, while O(1)–P–R(1) and R(1)–P–R(2) are narrowed by 3.3(2)° and 8.7(2)° relative to the expected 120.0° value; the value of 160.6(1)° for the angle O(2)–P–C(1) is also significantly smaller than the ideal value of 180.0°. In **2b**, the coordination of the phosphorus atom is closer to a tbp: deviations of the equatorial bond angles from the ideal value do not exceed 4.5(2)°, while the axial bond angle O(2)–P–C(1) is smaller than the ideal value by only 9.9(2)°. On the basis of the Berry coordinates [9] calculated from the sum of the dihedral angles between the polytopal faces using observed bond lengths, molecules **2a** and **2b** may be placed between the two idealized geometries, being displaced by 43.0% and 19.8% respectively from a trigonal bipyramid toward a square pyramid. The five-membered ring in both structures is non-planar, with O(1) and C(3) lying above (by 0.043 and 0.205 Å in **2a**, by 0.057 and 0.202 Å in **2b**), and O(2) and C(2) below (by 0.068 and 0.184 Å in **2a** and by 0.053 and 0.205 Å in **2b**) the least-squares plane, while the phosphorus atom lies in the plane. In both molecules this ring has an approximate half-chair (twist) conformation: the modified Cremer–Pople parameters [10] Q and ψ_2 are equal to 0.42 and 39.5° for **2a** and 0.43 and 215.1° for **2b** (for the ideal half-chair conformation $\psi_2 = 36.0 \times n$; for the ideal envelope conformation $\psi_2 = 36 \times n + 18$, where $n = 1, 2, 3$ [10]). The endocyclic apical and equatorial P–O bond lengths in **2a** are 1.760(2) and 1.693(2) Å, respectively, which are somewhat longer not only than the corresponding values of 1.712(2) and 1.649(2) Å for **2b** but also than the previously reported values of

1.685–1.715(3) and 1.613–1.648(3) Å for heterocycles of this type [11–15]. As a result of this elongation the value for the O(1)–P–O(2) angle in **2a** [84.90(8)°] is somewhat smaller than the corresponding value of 87.79(9)° in **2b** and the angle range of 86.7–91.9° in compounds of this type studied earlier [11–15]. The differences between the O(1)–C(2) and O(2)–C(3) bond lengths [0.021(3) Å in **2a** and 0.012(3) Å in **2b**], as well as between the P–O(1)–C(2) and P–O(2)–C(3) bond angles [2.4(1)° in **2a** and 1.8(1)° in 2b], reflect the degree of residual tbp character of the ring system. The increase in the P–C(1) bond length of 1.968(2) Å in **2a** is not unusual for phosphoranes with F_3C groups in apical positions [16]. It is noteworthy that in both structures the C(1)–F average bond lengths (1.346 Å in **2a** and

TABLE 3

The main geometrical parameters of **2a** [R=O(Et)] and **2b** [R=N(Et_2)]

	2a	**2b**
Bond lengths (Å)		
P–O(1)	1.693(2)	1.649(2)
P–O(2)	1.760(2)	1.712(2)
P–R(1)	1.645(2)	1.559(2)
P–R(2)	1.652(2)	1.560(2)
P–C(1)	1.968(2)	1.886(3)
O(1)–C(2)	1.397(3)	1.402(3)
O(2)–C(3)	1.376(3)	1.390(3)
C(2)–C(3)	1.615(3)	1.600(3)
C(1)–F(av.)	1.346(4)	1.349(3)
C(4,5,6,7)–F(av.)	1.328(4)	1.323(3)
Bond angles (°)		
O(1)–P–O(2)	84.90(8)	87.79(9)
O(1)–P–R(1)	116.7(2)	118.57(9)
O(1)–P–R(2)	132.0(2)	124.5(1)
O(1)–P–C(1)	78.2(2)	83.9(1)
O(2)–P–R(1)	99.43(9)	96.87(9)
O(2)–P–R(2)	88.41(8)	93.35(9)
O(2)–P–C(1)	160.6(1)	171.1(2)
R(1)–P–R(2)	111.3(2)	116.3(2)
R(1)–P–C(1)	96.7(1)	90.0(2)
R(2)–P–C(1)	95.8(2)	88.7(2)
P–O(1)–C(2)	121.6(1)	119.5(1)
P–O(2)–C(3)	119.2(1)	117.7(1)
O(1)–C(2)–C(3)	102.6(2)	102.8(2)
O(2)–C(3)–C(2)	103.2(2)	103.0(2)
Torsion angles (°)		
O(2)–P–O(1)–C(2)	−10.2(3)	11.7(2)
P–O(1)–C(2)–C(3)	24.5(3)	−26.5(2)
O(1)–C(2)–C(3)–O(2)	−28.4(3)	29.8(2)
C(2)–C(3)–O(2)–P	25.9(3)	−25.7(2)
C(3)–O(2)–P–O(1)	−11.9(3)	10.9(2)

1.349 Å in **2b**) are somewhat greater than the other average C–F bond lengths (1.328 Å in **2a** and 1.323 Å in **2b**).

Experimental

The appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work. Elemental analyses were undertaken by Mikroanalytisches Laboratorium Beller, Göttingen. Mass spectra were obtained on an MAT 8222 spectrometer (EI, electron energy 70 eV) while infrared spectra were obtained using a Nicolet 5 DX FT spectrometer with the spectra recorded as films between NaCl plates. NMR spectra were obtained on Bruker AC 80 and WH 360 instruments operating at 80.13 MHz (^{1}H, internal standard TMS), 75.39 MHz (^{19}F, internal standard CCl_3F), 32.44 MHz (^{31}P, external standard 85% H_3PO_4) and 90.54 MHz (^{13}C, internal standard TMS), respectively. Compounds **1a** and **1b** were synthesized using literature procedures [2, 3].

General method (see Table 4)

Hexafluoroacetone was condensed at −196 °C into a thick-walled glass tube containing the phosphonous acid derivative. The tube was allowed to warm slowly to 20 °C, stirred and opened at −196 °C. Traces of unchanged hexafluoroacetone were removed at 0 °C by gentle pumping. The crude product was distilled or recrystallized from methylcyclohexane.

*Crystal structure analysis of **2a** and **2b***

The X-ray structural study of compounds **2a** and **2b** was performed on a CAD-4-ENRAF-NONIUS diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ nm, the ratio of the scanning rates $\omega/\theta = 1.2$). The main crystallographic data for **2a** and **2b** are listed in Table 5. Both structures

TABLE 4

Experimental details for the preparation of compounds **2a**, **2b**, **4** and **5** (HFA = hexafluoracetone)

Compound	Reactants [g (mmol)]	Reaction conditions	Yield [g (%)]	B.p. (°C/mmHg); m.p. (°C)
2a	**1a**, 0.95 (5); HFA, 1.66 (10)	Warmed up for 24 h	1.40[a] (54)	43–44
2b	**1b**, 2.44 (10); HFA, 3.32 (20)	Warmed up for 2 h	5.31[a] (92)	75–76
4	**3a**, 2.00 (8); HFA, 2.66 (16)	Held at room temp. for 3 d	4.10 (88)	42/0.001
5	**3b**, 2.90 (10); HFA, 1.58 (10)	Held at room temp. for 12 h	3.91 (87)	50/0.001

[a]Recrystallized from methylcyclohexane.

TABLE 5

Crystal and data reduction parameters for **2a** and **2b**

	2a	**2b**
Formula	$C_{15}H_{20}F_{15}N_2O_2P$	$C_{11}H_{10}F_{15}O_4P$
Formula weight	576.3	522.2
$F(000)$	580	1032
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$
a (Å)	8.442(3)	7.255(1)
b (Å)	13.505(3)	29.716(5)
c (Å)	9.829(3)	8.201(3)
β (°)	105.96(2)	93.09(2)
V (Å^3)	1077.4	1765.5
Z	2	4
D_{calc} (g cm^{-3})	1.78	1.96
μ (cm^{-1})	2.6	3.2
Temperature (°C)	−100	−85
θ_{max} (°) for data	27	24
Reflection number:		
total	2259	2760
unique	2096	2521
significant	1909	1722
Cut-off	$I > 2\sigma(I)$	$I > 3\sigma(I)$
R	0.0273 0.0275[a]	0.029
R_w	0.0381 0.0384[a]	0.037

[a]Discrepancy factors for the inverted structure.

were solved by direct methods and refined by full-matrix least-squares methods. All hydrogen atoms were located in the difference Fourier maps. The hydrogen atoms in **2a** were included in the final refinement with the fixed positional and thermal ($B_{iso} = 4$ Å^2) parameters, whereas in **2b** the hydrogen atoms were refined isotropically. Corrections for Lorentz and polarization effects but not for absorption were applied. All structural calculations were carried out on a PDP-11/23+ computer using the SDP-PLUS programme package [17]. (The atomic coordinates are listed in Tables 6 and 7).

Analytical data

*2,2-Diethoxy-2-trifluoromethyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2$\lambda^5\sigma^5$-dioxaphospholane (**2a**)*

Mass spectrum (50 °C) m/z (%): 522 (M^+, 1); 503 ($M^+ - F$, 12); 477 ($M^+ - OC_2H_5$, 85); 453 ($M^+ - CF_3$, 90); 425 ($M^+ - OCCF_3$, 78); 397 ($M^+ - OCCF_3 - C_2H_4$, 100); 317 ($C_6F_{12}OH^+$, 24); 191 ($HP(CF_3)(OC_2H_5)_2{}^+$, 44); 137 ($OP(OC_2H_5)_2{}^+$, 48); 109 ($C_2F_3H^+$, 52); 69 ($CF_3{}^+$, 8); and other fragments. $C_{11}H_{10}F_{15}O_4P$ (522.14): Found: C, 25.30; H, 1.89; F, 54.6; P, 5.88%. Calcd.: C, 25.25; H, 1.92; F, 54.6; P, 5.94%.

TABLE 6

Coordinates for non-hydrogen atoms and their equivalent isotropic temperature factors B_{eq} (Å^2) in structure **2a**

Atom	x	y	z	B_{eq} (Å^2)
P	0.24630(8)	0.173	0.27150(6)	1.55(1)
F(1)	0.5093(2)	0.2836(1)	0.4131(2)	3.17(4)
F(2)	0.2861(3)	0.3693(1)	0.3655(2)	3.55(4)
F(3)	0.3380(2)	0.2691(1)	0.5386(2)	3.22(4)
F(4)	0.3166(3)	0.4088(2)	−0.0373(3)	4.97(5)
F(5)	0.2016(3)	0.3120(2)	−0.2061(2)	5.63(6)
F(6)	0.0720(3)	0.3623(2)	−0.0593(2)	4.31(5)
F(7)	0.4955(2)	0.2119(2)	−0.0946(2)	4.11(4)
F(8)	0.5396(2)	0.1560(1)	0.1191(2)	3.13(4)
F(9)	0.5521(2)	0.3101(2)	0.0838(2)	3.90(4)
F(10)	−0.0556(2)	0.1891(2)	−0.2083(2)	3.85(4)
F(11)	−0.0966(2)	0.0714(2)	−0.0741(2)	3.81(4)
F(12)	−0.0748(2)	0.2193(2)	0.0019(2)	3.16(4)
F(13)	0.1340(3)	−0.0167(2)	−0.1302(2)	5.12(5)
F(14)	0.3827(2)	0.0310(2)	−0.0542(2)	3.60(4)
F(15)	0.2199(3)	0.1021(2)	−0.2349(2)	4.68(5)
O(1)	0.2806(2)	0.2613(1)	0.1609(2)	2.02(4)
O(2)	0.1975(2)	0.0968(1)	0.1202(2)	1.70(3)
N(1)	0.0658(3)	0.1748(2)	0.3049(2)	1.92(4)
N(2)	0.3632(3)	0.0824(2)	0.3582(2)	1.73(4)
C(1)	0.3486(4)	0.2784(2)	0.4048(3)	2.48(6)
C(2)	0.2838(4)	0.2390(2)	0.0230(3)	2.13(5)
C(3)	0.1742(3)	0.1393(2)	−0.0110(3)	1.95(5)
C(4)	0.2150(4)	0.3327(2)	−0.0709(3)	3.07(6)
C(5)	0.4699(4)	0.2288(2)	0.0312(3)	2.81(6)
C(6)	−0.0154(4)	0.1559(2)	−0.0748(3)	2.74(6)
C(7)	0.2297(4)	0.0627(3)	−0.1089(3)	3.07(7)
C(8)	−0.0290(4)	0.0810(2)	0.2860(3)	2.42(6)
C(9)	−0.1158(4)	0.0630(3)	0.4021(3)	3.52(7)
C(10)	−0.0348(4)	0.2663(2)	0.2943(3)	2.60(6)
C(11)	−0.0554(5)	0.3059(3)	0.4355(4)	3.82(7)
C(12)	0.3812(4)	0.0678(2)	0.5123(3)	2.29(5)
C(13)	0.5543(4)	0.0878(3)	0.6099(3)	3.03(7)
C(14)	0.4296(3)	−0.0045(2)	0.2987(3)	1.93(5)
C(15)	0.3161(4)	−0.0945(2)	0.2675(3)	2.62(6)

2,2-Bis(diethylamino)-2-trifluoromethyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2λ^{5}σ^5-dioxaphospholane (**2b**)

Mass spectrum (70 °C) m/z (%): 576 (M^+, −); 557 ($M^+ - F$, 8); 507 ($M^+ - CF_3$, 35); 504 ($M^+ - N(C_2H_5)_2$, 100); 454 (M^+-CF_2-$N(C_2H_5)_2$, 91); 191 ($CF_3P(F)N(C_2H_5)_2{}^+$, 8); 104 ($HPN(C_2H_5)_2{}^+$, 32); 72 ($N(C_2H_5)_2{}^+$, 38); 69 ($CF_3{}^+$, 30); and other fragments. $C_{15}H_{20}F_{15}N_2O_2P$ (576.21): Found: C, 31.05; H, 3.48; F, 49.2; P, 5.51%. Calcd.: C, 31.25; H, 3.47; F, 49.5; P, 5.38%.

TABLE 7

Coordinates of non-hydrogen atoms and their equivalent isotropic temperature factors B_{eq} (Å^2) in structure **2b**

Atom	x	y	z	B_{eq} (Å^2)
P	0.8409(1)	0.16135(2)	0.80624(8)	1.80(1)
F(1)	1.0372(2)	0.23717(5)	0.7624(2)	3.60(4)
F(2)	0.9082(2)	0.21125(6)	0.5403(2)	3.45(4)
F(3)	1.1506(2)	0.17954(5)	0.6478(2)	3.08(4)
F(4)	0.7287(3)	0.01528(6)	0.5385(2)	4.16(4)
F(5)	0.9929(2)	0.04116(6)	0.6181(2)	3.52(4)
F(6)	0.8677(3)	0.06318(6)	0.3946(2)	4.57(5)
F(7)	0.4888(2)	0.14262(5)	0.5824(2)	3.09(4)
F(8)	0.6366(2)	0.12336(6)	0.3789(2)	3.76(4)
F(9)	0.4481(2)	0.07650(6)	0.4779(2)	3.87(4)
F(10)	0.4534(2)	0.05652(6)	0.9977(2)	4.14(4)
F(11)	0.4522(3)	0.02481(6)	0.7630(2)	4.04(4)
F(12)	0.3538(2)	0.09236(6)	0.7883(2)	3.77(4)
F(13)	0.9905(2)	0.06462(5)	0.9072(2)	2.84(3)
F(14)	0.7843(3)	0.04971(6)	1.0727(2)	3.61(4)
F(15)	0.8114(2)	0.00724(5)	0.8652(2)	3.49(4)
O(1)	0.8554(2)	0.12666(6)	0.6505(2)	1.83(4)
O(2)	0.6956(2)	0.12331(6)	0.8892(2)	1.93(4)
O(3)	0.9949(3)	0.15975(6)	0.9462(2)	2.37(4)
O(4)	0.6992(3)	0.20069(6)	0.8134(2)	2.43(4)
C(1)	0.9909(4)	0.19889(9)	0.6836(3)	2.45(6)
C(2)	0.7327(4)	0.09031(9)	0.6335(3)	1.98(6)
C(3)	0.6803(4)	0.08099(9)	0.8174(3)	1.95(5)
C(4)	0.8328(4)	0.0518(1)	0.5453(4)	2.76(6)
C(5)	0.5721(4)	0.10791(9)	0.9159(3)	2.58(6)
C(6)	0.4816(4)	0.0635(1)	0.8410(4)	2.87(6)
C(7)	0.8195(4)	0.04958(9)	0.9159(3)	2.58(6)
C(8)	0.9713(4)	0.1538(1)	1.1223(3)	3.02(7)
C(9)	1.1562(5)	0.1467(1)	1.2024(4)	4.78(9)
C(10)	0.5347(4)	0.2038(1)	0.9096(4)	3.00(7)
C(11)	0.4708(4)	0.2511(1)	0.9001(4)	3.83(7)

2,2-Diethoxy-2-[(Z)-1,2,3,3,3-pentafluoropropenyl]-4,4,5,5-tetrakis-(trifluoromethyl)-1,3,2λ^{5}σ^5-dioxaphospholane (4)

Mass spectrum (20 °C) m/z (%): 585 ($M^+ + H$, 5); 565 ($M^+ - F$, 12); 555 ($M^+ - C_2H_5$, 4); 539 ($M^+ - OC_2H_5$, 10); 511 ($M^+ - OC_2H_5 - C_2H_4$, 86); 459 ($M^+ - 2C_2H_4 - CF_3$, 50); 453 ($M^+ - C_3F_5$, 38); 425 ($M^+ - C_3F_5 - C_2H_4$, 12); 397 ($M^+ - C_3F_5 - 2C_2H_4$, 100); 109 ($C_3F_3O^+$, 12); 93 ($C_3F_3^+$, $P(OH)OC_2H_5^+$, 23); 81 (C_2F_3, 12); 69 (CF_3^+, 95); 65 ($P(OH)_2^+$, 40); 45 ($OC_2H_5^+$, 18); 29 ($C_2H_5^+$, 80); and other fragments. IR (cm^{-1}): 1689 (C=C). $C_{13}H_{10}F_{17}O_4P$ (584.17): Found: C, 26.54; H, 1.70; F, 55.6; P, 5.30%. Calcd.: C, 26.73; H, 1.73; F, 55.3; P, 5.28%.

2,2-Bis(diethylamino)-2,3-difluoro-4,5,5-tris(trifluoromethyl)-1,2-$\lambda^5\sigma^5$-oxaphospholene-(3) (5)

Mass spectrum (20 °C) *m/z* (%): 453 ($M^+ - F$, 35); 400 ($M^+ - NC_2H_5$, 100); 372 ($M^+ - NC_2H_5 - C_2H_4$, 6); 72 ($N(C_2H_5)_2{}^+$, 22); and other fragments. IR (cm^{-1}): 1677 (C=C). $C_{14}H_{20}F_{11}N_2OP$ (472.28): Found: C, 35.46; H, 4.21; F, 44.50; P, 6.56%. Calcd.: C, 33.61; H, 4.27; F, 44.25; P, 6.49%.

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