Reaction of 5-oxo-2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,2-benzodioxaphosphepine with chloral. The synthesis and spatial structure of 5-carbaphosphatrane containing a four-membered ring

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Phosphorylation of 2-hydroxyphenyl 2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl ketone with dichloro(phenyl)phosphine gave 5-oxo-2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,2-benzodioxaphosphepine. Heating of the latter initiated an intramolecular interaction of the P atom with the carbonyl group. Hydrolysis of the intermediate product yielded 3-hydroxy-2-oxo-2-phenyl-3-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]-2,3-dihydro-1,2λ^5-benzo[*d*]oxaphosphole. The reaction was highly stereoselective (P_RC_S/P_SC_R). The reaction of the starting phosphepine with chloral proceeded highly stereoselectively ($P_RC_SC_S/P_SC_RC_R$) to give a 5-carbaphosphatrane derivative containing a four-membered ring, namely, 1-phenyl-3-trichloromethyl-10,10-bis(trifluoromethyl)-6,7-benzo-2,4,8,9-tetraoxa-1λ^5-phosphatricyclo[3.3.2.0^{1,5}]decene. The trigonal bipyramid of the 5-carbaphosphatrane derivative is made up of the equatorial O atoms and the apical C atoms.

Key words: dioxaphosphepine, chloral, phosphorane, carbaphosphatrane, benzophosphole, trigonal bipyramid, apicophilicity, oxaphosphetane, stereoselectivity.

Phosphoranes (compounds with a pentacoordinated phosphorus atom) are intermediates in phosphorylation and dephosphorylation of important natural hydroxy-containing compounds. That is why their synthesis, reactivities, and configurational stabilities are under intensive study.[1—12] The benzodioxaphosphole fragment stabilizes the pentacoordinated state of phosphorus most efficiently.[5] Taking this into account, we have proposed a new approach to the preparation of phosphoranes that involves reactions of activated carbonyl compounds with benzodioxaphospholes containing the tricoordinated P atom and a carbonyl or imino group in the γ- or δ-position relative to the P atom in the endocyclic substituent. This approach allowed highly regio- and stereoselective synthesis of unusual framework-type phosphoranes with several chiral centers.[13—17]

Results and Discussion

In the present work, we continued to develop this approach by using P^{III} derivatives with the endocyclic γ-carbonyl group as objects of investigations. For instance, base-catalyzed phosphorylation of hydroxy ketone **1** (see Ref. 18) with dichloro(phenyl)phosphine gave seven-membered P-heterocycle **2**, which contains the nucleophilic P atom along with the carbonyl group activated by the electron-withdrawing *gem*-bis(trifluoromethyl) fragment. Structure **2** was identified by ^{1}H, ^{19}F, and ^{31}P NMR and IR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum shows a characteristic quartet of quartets at δ_P 173.1. The trifluoromethyl groups are nonequivalent: their ^{19}F NMR signals appear as two multiplets at δ_F −73.5 and −74.0.

Benzophosphepinone **2** is fairly stable in an inert atmosphere; however, it is oxidized with atmospheric oxygen to $\sigma^5\lambda^4$-phosphepine (**3**) (δ_P 14.9). The IR spectrum of compound **3** shows an band absorption at 1288 cm^{-1} (P=O). The trifluoromethyl groups remain nonequivalent: their ^{19}F NMR signals appear as two quartets at δ_F −73.57 and −74.13 ($^4J_{F,F}$ = 9.2 Hz).

When heated or kept in CH_2Cl_2 (20 °C) for a long period of time, benzophosphepinone **2** undergoes an intramolecular transformation leading to a compound with a chemical shift δ_P of 60.4. One could assume that the product is tricyclic spiro compound **4** resulting from an

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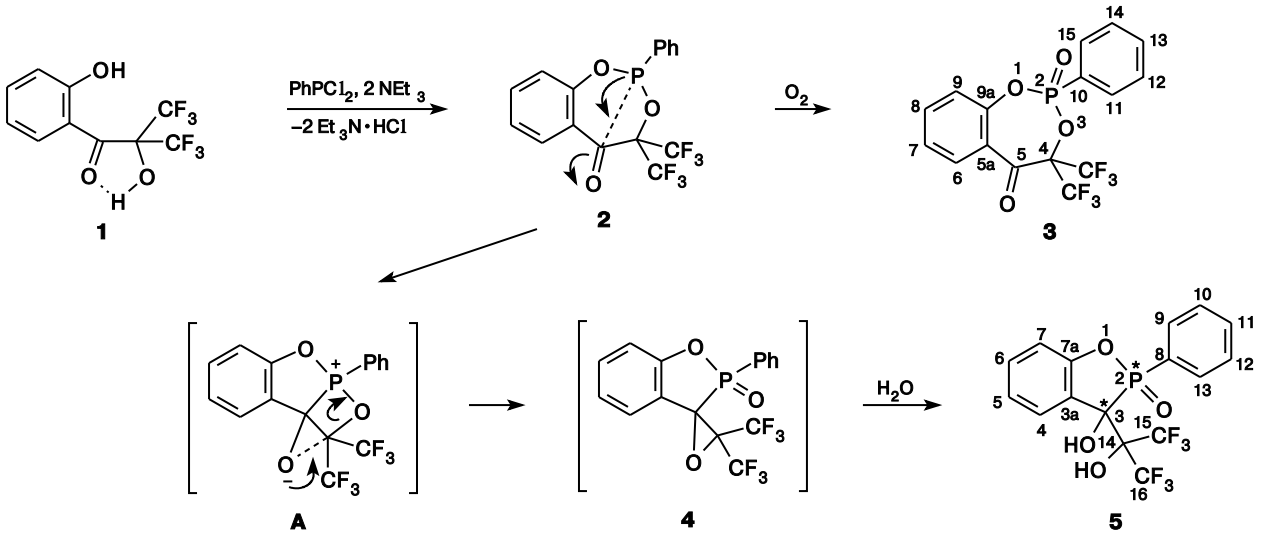
Scheme 1



attack of the P atom on the C atom of the endocyclic carbonyl group (intermediate zwitterion **A**, Scheme 1). However, the compound isolated from the reaction mixture intensely absorbs in the range characteristic of hydroxy groups (3074, 2798 cm^{-1}). According to ^{31}P, $^{13}C\{^1H\}$, ^{13}C, and ^1H NMR and IR spectra, the product is diol **5**. Its molecular formula was confirmed by mass spectra and elemental analysis data.

Diol **5** contains two chiral centers; however, this compound forms only one diastereomer, which suggests the high stereoselectivity of both the intramolecular cyclization (because of the rigid cyclic structure of the starting regent **2**) and the hydrolysis of intermediate oxirane **4**. The relative configurations of the chiral centers of structure **5** were determined by X-ray diffraction. The crystal structure **5** is shown in Fig. 1; its selected geometrical parameters are given in Table 1. The phospholane ring has an envelope conformation; the P(2) atom deviates from the plane O(1)C(7a)C(3a)C(3) by 0.56 Å. The phenyl substituent at the P atom is in the equatorial position, while the phosphoryl group is axial.

The observed conformation of the molecule is stabilized by intramolecular hydrogen bonds. The hydroxy group at the C(3) atom is linked with the phosphoryl group by the most significant H-bond with the following parameters: *d*(O(3)—H(3)), 0.88(3) Å, *d*(H(3)···O(2)), 2.28(4) Å, *d*(O(3)···O(2)), 2.802(3) Å, angle O(3)—H(3)···O(2), 118(4)°. Intermolecular interactions in the crystal structure **5** include both classic hydrogen bonds and the bonds C—H···F, C—H···O, and O—H···F. The classic hydrogen bond O(4)—H(40)···O(2′) unites molecules into a chain aligned with the crystallographic axis 0*c*; the hydrogen bond O(3)—H(3)···F(5″) involving the fluorine atom form chains along the same direction (Fig. 2). The parameters of these bonds are as follows: *d*(H(40)···O(2′)), 1.66(5) Å, *d*(O(4)···O(2′)), 2.599(3) Å, angle O(4)—H(40)···O(2′), 175(5)° (the symmetry operation code is x, $1/2-y$, $1/2+z$) and *d*(H(3)···F(5″)), 2.32(4) Å, *d*(O(3)···F(3″)), 3.112 (2) Å, angle O(3)—H(3)···F(5″), 150(4)° (x, $1/2-y$, $-1/2+z$). The hydrogen bond between the H(4) atom of the fused benzene fragment and the O(3) atom of the hydroxy group unites adjacent chains related by a center of symmetry along the axis 0*b* to form a supramolecular bilayer structure (Fig. 3). The parameters of the hydrogen bond C(4)—H(4)···O(3‴) ($1-x$, $1-y$, $-z$) are *d*(H(4)···O(3‴)), 2.58 Å, *d*(C(4)···O(3‴)), 3.521(4) Å, and angle C(4)—H(4)···O(3‴), 169°. The bilayers are parallel to the crystallographic plane 0*bc*. Their external sides bear the phenyl fragments so that these bilayers are held together in the crystal only by van der Waals and probably π—π interactions. The interplanar spacings between the fused benzene rings of adjacent (related by a center of symmetry) molecules are 3.744 Å and those between the

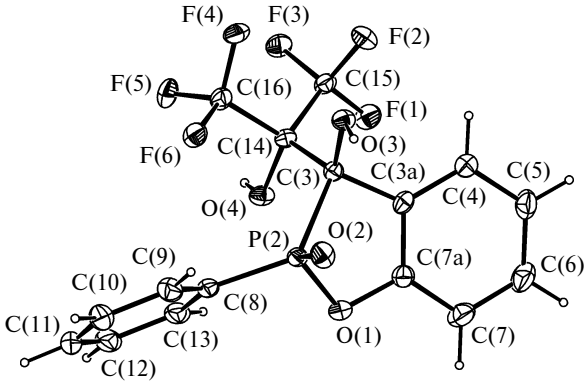


Fig. 1. Crystal structure of phosphole **5**.

Table 1. Selected bond lengths (*d*), bond angles (ω), and torsion angles (θ) in structure **5**

Parameter	Value	Parameter	Value	Parameter	Value
Bond length	*d*/Å	Bond angle	ω/deg	Bond angle	ω/deg
P(2)—O(2)	1.482(2)	O(2)—P(2)—O(1)	115.3(1)	C(3A)—C(3)—C(14)	113.9(2)
P(2)—O(1)	1.613(2)	O(2)—P(2)—C(8)	111.3(1)	O(3)—C(3)—P(2)	110.3(2)
P(2)—C(8)	1.780(2)	O(1)—P(2)—C(8)	103.6(1)	C(3A)—C(3)—P(2)	96.7(2)
P(2)—C(3)	1.899(2)	O(2)—P(2)—C(3)	103.4(1)	C(14)—C(3)—P(2)	114.1(2)
O(4)—C(14)	1.390(3)	O(1)—P(2)—C(3)	96.5(1)	Torsion angle	θ/deg
O(1)—C(7A)	1.405(3)	C(8)—P(2)—C(3)	126.4(1)		
O(3)—C(3)	1.412(3)	C(7A)—O(1)—P(2)	108.3(1)	O(1)—P(2)—C(8)—C(9)	138.8(2)
C(3A)—C(7A)	1.390(3)	C(4)—C(3A)—C(3)	126.9(2)	O(1)—P(2)—C(8)—C(13)	−37.9(2)
C(3A)—C(3)	1.535(3)	C(7A)—C(3A)—C(3)	114.0(2)	O(4)—C(14)—C(3)—O(3)	−163.8(2)
C(14)—C(3)	1.553(3)	O(3)—C(3)—C(3A)	113.3(2)	O(4)—C(14)—C(3)—P(2)	−40.5(2)
		O(3)—C(3)—C(14)	108.4(2)	C(15)—C(14)—C(3)—P(2)	−161.3(2)

planes of the phenyl substituents (related by another center of symmetry) is 3.337 Å.

In the crystal of compound **5**, fluorine-containing fragments of the molecules are localized as described earlier.[19] In this case, these fragments virtually make up layers with intermolecular (2.907(2)—3.126(2) Å) and intramolecular F···F contacts (2.666(2)—2.828(2) Å). The packing factor is 68.8.

A reaction of dioxaphosphepinone **2** with reactive chloral (Scheme 2) unexpectedly gives a 5-carbaphosphatrane derivative, namely, 1-phenyl-3-trichloromethyl-10,10-bis(trifluoromethyl)-6,7-benzo-2,4,8,9-tetraoxa-1λ^5-phosphatricyclo[3.3.2.0^{1,5}]decene (**6**) (δ_P 4.6). This compound is a first representative of carbaphosphatranes containing a four-membered ring annulated with two five-membered rings along the P—C bond. Earlier,[20—23] carbaphosphatranes with five- and six-membered rings annulated along the P—C bond have been documented.

Apparently, the reaction involves an intramolecular attack of the P atom on the endocyclic carbonyl group with a simultaneous interaction of the P atom with the O atom of chloral. The resulting zwitterion (**B**) undergoes cyclization into carbaphosphatrane **6**. During the reaction, two chiral centers are formed from two prochiral carbonyl C atoms.

Structure **6** was identified by NMR spectroscopy; its molecular formula was confirmed by elemental analysis. In the ^{1}H NMR spectrum, a signal for the HC(3) proton appears as a doublet at δ 5.77 ($^3J_{P,H}$ = 7.3 Hz). The spatial structure of compound **6** in the crystal is shown in Fig. 4 (X-ray diffraction data). Its selected geometrical parameters are given in Table 2. The coordination polyhedron of the P atom is a slightly distorted trigonal bipyramid with three equatorial O(2), O(8), and O(9) atoms (the sum of the bond angles O—P—O is 359.3°); the configuration of the chiral centers is P(1)$_R$C(3)$_S$C(5)$_S$/P(1)$_S$C(3)$_R$C(5)$_R$ (the configuration of the P atom was determined from earlier cited[24] data). The peculiarity of this structure

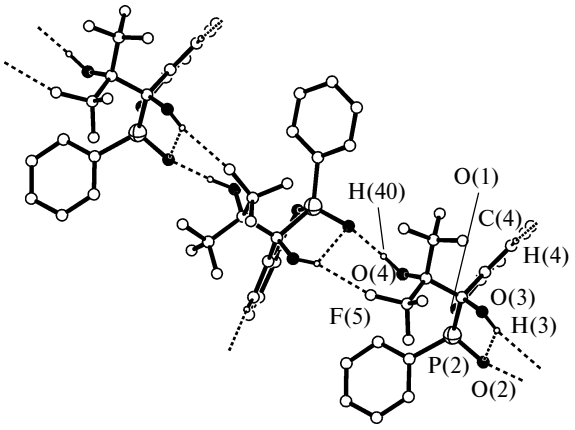


Fig. 2. Fragment of an H-bonded chain of phosphole molecules **5** in the crystal as viewed along the axis 0*a*. The hydrogen atoms involved in hydrogen bonding are shown only (dashed lines).

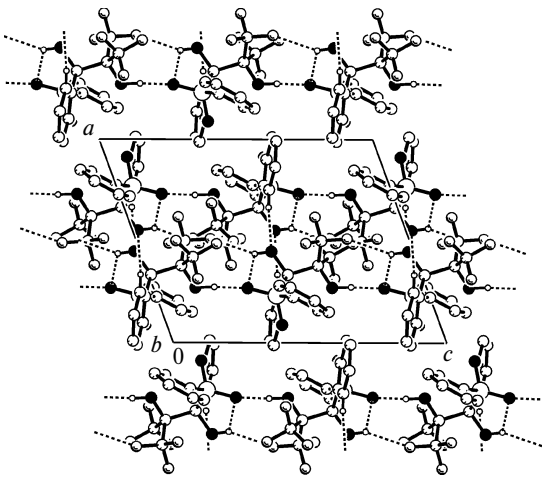
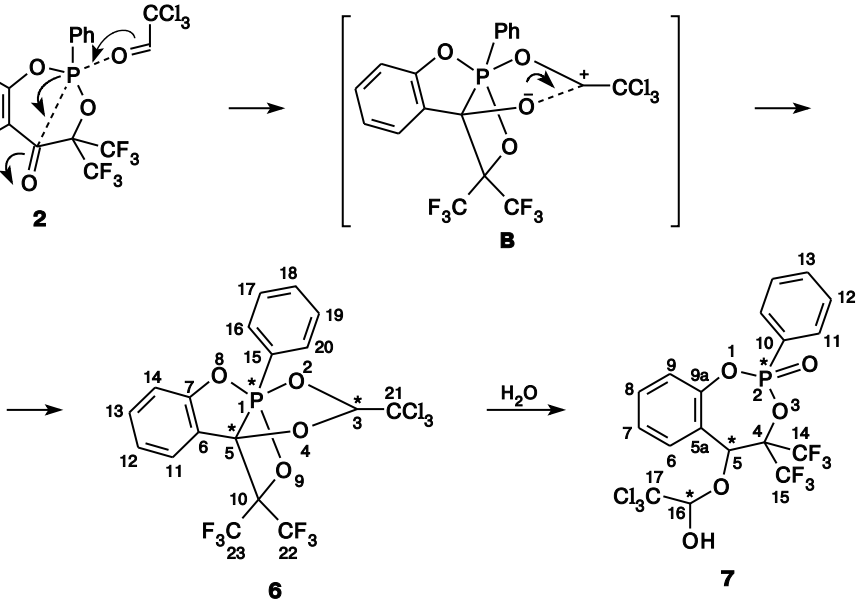


Fig. 3. Supramolecular bilayer structure in the crystal of phosphole **5** as viewed along the axis 0*b*. The hydrogen atoms involved in hydrogen bonding are shown only (dashed lines).

Scheme 2



is the axial arrangement of the bonds P(1)—C(5) and P(1)—C(15), which is in conflict with the apicophilicity rule. The bond angle C(5)—P(1)—C(15) is 173.7(4)°. The P—C bond lengths differ appreciably: the bridging P(1)—C(5) bond of the tricyclic system (1.933(8) Å) is strongly lengthened, while the exocyclic P(1)—C(15) bond (1.811(9) Å) has a normal value. Apparently, this is because the P(1)—C(5) bond is part of the strained four-membered ring. The P—O bonds also differ in length: P(1)—O(9) in the four-membered ring is the longest bond (1.655(8) Å), P(1)—O(2) in the dioxaphospholane ring is the shortest bond (1.563(7) Å), and P(1)—O(8) in the oxaphospholane ring is the intermediate bond (1.610(8) Å).

The oxaphosphetane, oxaphospholane, and dioxaphospholane rings are planar within the experimental errors (for the corresponding torsion angles, see Table 2); the dihedral angles between their planes are about 60°, which also provides evidence for the nearly ideal trigonal-bipyramidal coordination of the P atom. Unfortunately, the quality of the crystal of compound **6** prevents more detailed discussion of the geometry of this molecule because of the large error of its geometrical parameters.

In the absence of strong intermolecular interactions, the molecular packing in the crystal of compound **6** mainly depends on van der Waals interactions. The distances between the parallel benzene rings of adjacent molecules (3.170 and 3.661 Å) correspond to weak interactions of aromatic systems (Fig. 5). In the crystal, halogen—halogen areas are also localized. The interatomic F···F distances range from 2.99 to 3.33 Å for intermolecular con-

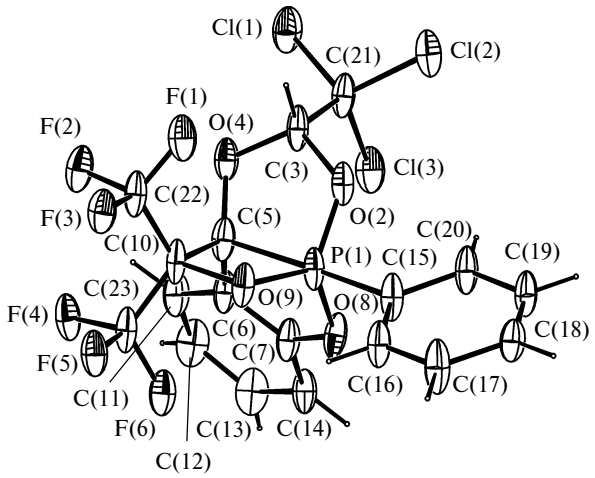


Fig. 4. Crystal structure of carbaphosphatrane **6**.

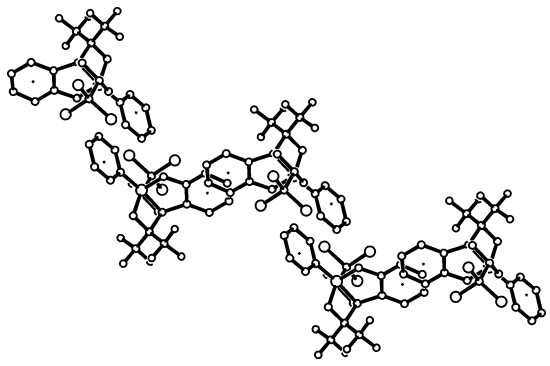


Fig. 5. Chain of molecules **6** along the axis 0*c*.

Table 2. Selected bond lengths (*d*), bond angles (ω), and torsion angles (θ) in structure **6**

Parameter	Value
Bond length	*d*/Å
C(3)—O(4)	1.42(1)
C(3)—O(2)	1.44(2)
C(5)—O(4)	1.42(2)
C(5)—C(6)	1.52(2)
C(5)—C(10)	1.56(1)
C(5)—P(1)	1.93(1)
C(6)—C(7)	1.38(2)
C(7)—O(8)	1.41(1)
C(10)—O(9)	1.47(1)
C(15)—P(1)	1.811(9)
O(2)—P(1)	1.56(1)
O(8)—P(1)	1.610(9)
O(9)—P(1)	1.655(6)
Bond angle	ω/deg
C(6)—C(5)—P(1)	104.3(8)
C(10)—C(5)—P(1)	86.4(6)
C(7)—C(6)—C(5)	111.2(8)
O(9)—C(10)—C(5)	95.9(6)
C(3)—O(2)—P(1)	120.8(7)
C(3)—O(4)—C(5)	108.8(9)
C(7)—O(8)—P(1)	116.1(7)
C(10)—O(9)—P(1)	100.4(5)
O(2)—P(1)—O(8)	121.9(5)
O(2)—P(1)—O(9)	117.8(5)
O(8)—P(1)—O(9)	118.5(5)
O(2)—P(1)—C(15)	94.7(5)
O(8)—P(1)—C(15)	92.0(4)
O(9)—P(1)—C(15)	96.5(4)
O(2)—P(1)—C(5)	87.3(6)
O(8)—P(1)—C(5)	92.0(5)
O(9)—P(1)—C(5)	77.3(4)
C(15)—P(1)—C(5)	173.7(4)
Torsion angle	θ/deg
O(2)—C(3)—O(4)—C(5)	−4(1)
P(1)—C(5)—O(4)—C(3)	3.1(8)
C(3)—O(2)—P(1)—C(5)	−0.7(7)
C(20)—C(15)—P(1)—O(9)	−158.9(7)
O(4)—C(5)—P(1)—O(2)	−1.5(6)
C(6)—C(5)—P(1)—O(2)	119.7(8)
C(10)—C(5)—P(1)—O(2)	−119.2(8)
O(4)—C(5)—P(1)—O(8)	−123.4(7)
C(6)—C(5)—P(1)—O(8)	−2.2(9)
C(10)—C(5)—P(1)—O(8)	118.9(9)
O(4)—C(5)—P(1)—O(9)	117.8(7)
C(6)—C(5)—P(1)—O(9)	−121.0(9)

tacts and from 2.57 to 2.71 Å for intramolecular ones. The localization gives rise to island-type associates (the packing factor is 66.5).

Compound **6** undergoes slow hydrolysis in several pathways. One pathway leads to the formation of dioxaphosphepine **7** resulting from cleavage of the P—C bond. Compound **7** was isolated by crystallization and characterized by NMR and IR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum shows the corresponding singlet at δ_P 6.5. The IR spectrum exhibits a wide band at 3280 cm^{-1} due to the OH stretches.

To sum up, the use of P^{III} derivatives containing an endocyclic carbonyl group in the γ-position relative to the P atom in reactions with chloral allows the synthesis of unusual framework phosphoranes. These are carbaphosphatrane derivatives containing a four-membered cycle, such as 1-phenyl-3-trichloromethyl-10,10-bis(trifluoromethyl)-6,7-benzo-2,4,8,9-tetraoxa-1λ^5-phosphatricyclo[3.3.2.0^{1,5}]decene.

Experimental

NMR spectra were recorded on Varian Unity-300 (300 (^{1}H), 121.42 ($^{31}P\{^1H\}$), and 282.4 MHz (^{19}F)) and Bruker Avance-600 instruments (600 (^{1}H), 242.8 ($^{31}P\{^1H\}$), and 150.9 MHz (^{13}C,$^{13}C\{^1H\}$)). IR spectra were recorded on a Bruker Vector-22 FTIR spectrometer (KBr pellets or neat samples). Mass spectra were measured on a TRACE MS Finnigan MAT instrument (EI, 70 eV, direct inlet probe, ionization chamber temperature 200 °C). The evaporating tube was heated in a programmed mode from 35 to 150 °C at a rate of 35 deg min^{-1}. In the mass spectra, the peaks of the ions containing the most commonly encountered isotopes are included.

5-Oxo-2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,2-benzodioxaphosphepine (2). A solution of dichloro(phenyl)-phosphine (2.74 g, 0.015 mol) in ether (20 mL) was added dropwise under argon at −30 °C to a mixture of 2-hydroxyphenyl 2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl ketone (**1**) (4.41 g, 0.015 mol) and triethylamine (3.1 g, 0.031 mol) in ether (75 mL). The reaction mixture was stirred for 1.5 h until it was warmed to 20 °C and then kept for ~14 h. The precipitate of triethylammonium chloride that formed was filtered off, the filtrate was concentrated, and the residue was dried *in vacuo* (20 °C, 0.1 Torr) to produce a fine crystalline solid. The yield was 5.49 g (91%), m.p. 104—107 °C (decomp.). ^{19}F NMR ($CDCl_3$), δ: −73.57 (dq, CF^A_3, $^4J_{POCCF(A)}$ = 20.5 Hz, $^4J_{F(B)CCCF(A)}$ = 9.2 Hz), −74.13 (dq, CF^B_3, $^4J_{F(A)CCCF(B)}$ = = 9.2 Hz, $^4J_{POCCF(B)}$ = 2.3 Hz). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$), δ_P: 173.1 (qq, $^4J_{POCCF(A)}$ = = 20.7 Hz, $^4J_{POCCF(B)}$ = = 2.5 Hz). IR, ν/cm^{-1}: 1684, 1600, 1444, 1288, 1164, 1128, 1064, 976, 896, 872, 776, 744, 712, 689.

Oxidation of compound 2 with oxygen was carried out by bubbling dried oxygen through a solution of compound **2** in CH_2Cl_2 at 20 °C for 2 h. The solvent was removed and the residue was crystallized from hexane to give 2,5-dioxo-2-phenyl-4,4-bis-(trifluoromethyl)-4,5-dihydro-1,3,2λ^5-benzodioxaphosphepine (**3**). The yield was 89%, colorless crystalline precipitate, m.p. 82 °C. Found (%): C, 46.77; H, 2.41; P, 7.49. $C_{16}H_9F_6O_4P$. Calculated (%): C, 46.83; H, 2.20; P, 7.56. $^{31}P\{^1H\}$ NMR (242.8 MHz, acetone-d_6), δ_P: 15.9. ^{1}H NMR (600 MHz, acetone-d_6), δ: 7.21 (d, H(9), $^3J_{H(8)H(9)}$ = 8.2 Hz); 7.54 (dd, H(7), $^3J_{H(6)H(7)}$ = 7.9 Hz, $^3J_{H(8)H(7)}$ = 7.7 Hz); 7.69 (br.ddd, H(12), $^3J_{H(11)H(12)}$ = 8.2—8.3 Hz, $^3J_{H(13)H(12)}$ = 7.5—7.6 Hz, $^4J_{PH(12)}$ = = 5.1 Hz); 7.84 (br.tm, H(13), $^3J_{H(12)H(13)}$ = 7.5—7.6 Hz, $^4J_{H(11)H(13)}$ = 2.2 Hz, $^5J_{PH(13)}$ = 1.2 Hz); 7.80 (br.dd, H(8), $^3J_{H(7)H(8)}$ = 7.7 Hz, $^3J_{H(9)H(8)}$ = 8.2 Hz); 7.90 (dd, H(6), $^3J_{H(7)H(6)}$ = 7.9 Hz, $^4J_{H(8)H(6)}$ = 1.7 Hz); 7.95 (br.ddd, H(11), $^3J_{PH(11)}$ = 14.5 Hz, $^3J_{H(12)H(11)}$ = 8.3 Hz, $^4J_{H(13)H(11)}$ = 2.2 Hz). ^{13}C NMR (acetone-d_6), δ (hereafter, the shapes of the signals in the $^{13}C\{^1H\}$ NMR spectrum are given in square brackets): 79.67 (septq [septq], C(4), $^2J_{FCC(4)}$ = 29.3 Hz, $^2J_{POC(4)}$ = 7.2 Hz); 182.14 (br.s [s], C(5)), 123.98 (br.m [s], C(5a)); 128.37 (ddd [s], C(6), $^1J_{HC(6)}$ = 165.1 Hz, $^3J_{HC(8)CC(6)}$ = 8.3 Hz, $^2J_{HCC(6)}$ = 2.5 Hz);

123.14 (dd [s], C(7), $^1J_{HC(7)}$ = 166.4 Hz, $^3J_{HC(9)CC(7)}$ = 7.7 Hz); 133.80 (ddd [s], C(8), $^1J_{HC(8)}$ = 164.8 Hz, $^3J_{HC(6)CC(8)}$ = 8.8 Hz, $^2J_{HCC(8)}$ = 1.7 Hz); 118.18 (ddddd [d], C(9), $^1J_{HC(9)}$ = 167.0 Hz, $^3J_{POCC(9)}$ = 7.7 Hz, $^3J_{HC(7)CC(9)}$ = 7.7 Hz, $^2J_{HC(8)C(9)}$ = 1.2 Hz, $^4J_{HC(6)CCC(9)}$ = 1.2 Hz); 123.65 (br.dt [d], C(10), $^1J_{PC(10)}$ = = 196.8 Hz, $^3J_{HC(12)CC(10)}$ = 7.5 Hz); 128.55 (dddd [d], C(11), C(15), $^1J_{HC(11)}$ = 164.9 Hz, $^2J_{PCC(11)}$ = 11.1 Hz, $^3J_{HCCC(11)}$ = = 7.7—7.8 Hz, $^3J_{HCCC(11)}$ = 7.7 Hz); 125.76 (dddd [d], C(12), C(14), $^1J_{HC(12)}$ = 163.6 Hz, $^3J_{PCCC(12)}$ = 16.6 Hz, $^3J_{HC(14)CC(12)}$ = = 7.2 Hz, $^2J_{HCC(12)}$ = 1.7 Hz); 131.54 (br.dm [d], C(13), $^1J_{HC(13)}$ = = 159.8 Hz, $^3J_{HC(11)CC(13)}$ = 7.4—7.6 Hz, $^4J_{PCCCC(13)}$ = 2.8 Hz, $^2J_{HC(12)C(13)}$ = 2.5 Hz); 121.39 (q [q], CF_3, $^1J_{FC}$ = 287.5 Hz); 121.26 (qd [qd], CF_3, $^1J_{FC}$ = 288.0 Hz, $^3J_{POCC}$ = 9.4 Hz).

3-Hydroxy-2-oxo-2-phenyl-3-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]-2,3-dihydro-1,2λ^5-benzo[*d*]oxaphosphole (5). Phosphonite **2** (2.38 g, 0.01 mol) was heated in a sealed tube at 110 °C for 30 min. On cooling, the tube was opened and CH_2Cl_2 (2 mL) was added. The resulting precipitate was filtered off and recrystallized from acetone. The yield was 1.45 g (61%), colorless crystals, m.p. 148—149 °C. Found (%): C, 46.71; H, 2.91; P, 7.46. $C_{16}H_{11}F_6O_4P$. Calculated (%): C, 46.60; H, 2.67; P, 7.52. MS, *m/z* (I_{rel} (%)) (the peaks of the ions containing the most commonly encountered isotopes are cited): 412 $[M]^{+\cdot}$ (21.1), 395 [M – OH] (39.0), 394 $[M - H_2O]^+$ (52.3), 343 $[M - CF_3]^+$ (41.2), 326 $[M - CF_3 - OH]^+$ (10.0), 325 $[M - CF_3 - H_2O]^+$ (19.6), 247 $[M - (CF_3)_2CO + H]^+$ (31.2), 246 $[M - (CF_3)_2CO]^+$ (44.2), 245 $[M - (CF_3)_2CO - H]^+$ (52.3), 125 $[PhPOH]^+$ (16.4), 124 $[PhPO]^+$ (43.3), 121 $[C_6H_4CO(OH)]^+$ (100.0), 92 $[C_6H_4O]^+$ (54.4), 69 $[CF_3]^+$ (53.2). IR, ν/cm^{-1}: 3521 s, 3074 vbr, vs, 2798, 1822, 1681, 1611, 1587, 1460, 1441, 1420, 1346, 1286 s, 1256 s, 1225 vs, 1199 s, 1155—1170 vs, 1117 s, 1083 s, 1048 s, 1027 m, 977 s, 957 m, 882 s, 869 sh, 847 m, 837 m, 801 m, 760 s, 752 s, 736 m, 723 s, 712 s, 688 m, 668 m. ^{1}H NMR (600 MHz, acetone-d_6), δ: 6.30 (br.s, OH); 7.14 (d, H(7), $^3J_{H(6)H(7)}$ = 8.1 Hz); 7.27 (dd, H(5), $^3J_{H(4)H(5)}$ = 7.7 Hz, $^3J_{H(6)H(5)}$ = 7.6 Hz); 7.50 (ddd, H(6), $^3J_{H(7)H(6)}$ = 8.1 Hz, $^3J_{H(5)H(6)}$ = 7.6 Hz, $^4J_{H(4)H(6)}$ = 1.2 Hz); 7.54 (br.ddd, H(10), $^3J_{H(11)H(10)}$ = 7.5 Hz, $^3J_{H(9)H(10)}$ = 7.4 Hz, $^4J_{PCCCH(10)}$ = 4.4 Hz); 7.67 (br.s, OH); 7.68 (br.td, H(11), $^3J_{H(10)H(11)}$ = 7.5 Hz, $^4J_{H(9)H(11)}$ = 1.3—1.4 Hz); 7.67 (br.dd, H(4), $^3J_{H(5)H(4)}$ = 7.7 Hz, $^4J_{H(6)H(4)}$ = 1.1—1.2 Hz); 8.01 (dd, H(9), $^3J_{PH(9)}$ = 12.8—12.9 Hz, $^3J_{H(10)H(9)}$ = 7.4 Hz). ^{31}P{^{1}H} NMR (124.42 MHz, $CDCl_3$ + acetone-d_6 (30%)), δ_P: 61.1. ^{19}F NMR (acetone-d_6), δ: –68.33 (m, CF_3); –68.51 (m, CF_3). ^{13}C NMR (acetone-d_6), δ: 84.79 (d [d], C(3), $^1J_{PC(3)}$ = 93.4 Hz); 127.22 (m [d], C(3a), $^2J_{PCC(3a)}$ = = 14.9 Hz); 130.90 (br.dm [br.d], C(4), $^1J_{HC(4)}$ = 164.2 Hz, $^3J_{PCCC(4)}$ = 7.5 Hz); 125.50 (dd [s], C(5), $^1J_{HC(5)}$ = 162.5 Hz, $^3J_{HC(7)CC(5)}$ = 7.7 Hz); 133.64 (dd [s], C(6), $^1J_{HC(6)}$ = 162.0 Hz, $^3J_{HC(4)CC(6)}$ = 8.4 Hz); 116.03 (ddd [d], C(7), $^1J_{HC(7)}$ = 165.3 Hz, $^3J_{HC(5)CC(7)}$ = 7.8—8.0 Hz, $^3J_{POCC(7)}$ = 6.6 Hz); 155.22 (br.dd [d], C(7a), $^3J_{HC(4)CC(7a)}$ = 9.1 Hz, $^3J_{HC(6)CC(7a)}$ = 9.1 Hz, $^2J_{POC(7a)}$ = 1.4 Hz); 129.67 (dt [d], C(8), $^1J_{PC(8)}$ = 132.7 Hz, $^3J_{HC(10)CC(8)}$ = 8.6 Hz); 136.54 (dddd [d], C(9), $^1J_{HC(9)}$ = 165.3 Hz, $^2J_{PCC(9)}$ = 10.5 Hz, $^3J_{HC(11)CC(9)}$ = 7.7 Hz, $^3J_{HC(13)CC(9)}$ = 7.7 Hz); 129.48 (br.ddd [d], C(10), $^1J_{HC(10)}$ = 161.3 Hz, $^3J_{PCCC(10)}$ = = 14.9 Hz, $^3J_{HC(12)CC(10)}$ = 7.9—8.0 Hz); 135.12 (dm [d], C(11), $^1J_{HC(11)}$ = 158.5 Hz, $^3J_{HC(9)CC(11)}$ = 7.5 Hz, $^4J_{PCCCC(11)}$ = = 3.0 Hz); 82.46 (septd [septd], C(14), $^2J_{FCC(14)}$ = 27.7 Hz, $^2J_{PCC(14)}$ = 3.3 Hz); 124.38 (qd [qd], C(15), $^1J_{FC(15)}$ = 290.3 Hz, $^3J_{PCCC(15)}$ = 14.2 Hz); 124.79 (q [q], C(16), $^1J_{FC(16)}$ = 287.5 Hz, $^3J_{PCCC(16)}$ = 0 Hz).

1-Phenyl-3-trichloromethyl-10,10-bis(trifluoromethyl)-6,7-benzo-2,4,8,9-tetraoxa-1λ^5-phosphatricyclo[3.3.2.0^{1,5}]decene (6). A mixture of phosphonite **2** (2.76 g, 0.007 mol) and chloral (2.07 g, 0.014 mol) in CH_2Cl_2 (20 mL) was kept under argon at 20 °C for two months. The solvent was removed *in vacuo* and a residual yellow oil was dissolved in CH_2Cl_2—pentane (5 : 1) and kept under argon for six days, while allowing slow evaporation of the solvent. The yield of compound **6** was 1.78 g (47%), colorless crystals, m.p. 119 °C. Found (%): C, 39.83; H, 2.03; P, 5.66. $C_{18}H_{10}Cl_3F_6O_4P$. Calculated (%): C, 39.89; H, 1.85; P, 5.72. IR, ν/cm^{-1}: 1614, 1592, 1476, 1462, 1441, 1355, 1323, 1293, 1223, 1168, 1127, 1109, 1069, 1041, 1018, 1003, 973, 935, 893, 867, 853, 839, 825, 794, 774, 764, 746, 728, 693, 645, 630. ^{31}P{^{1}H} NMR (242.8 MHz, $CDCl_3$), δ_P: 4.6 (s). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 5.81 (d, H(3), $^3J_{PH(3)}$ = 7.1 Hz); 7.05 (br.d, H(14), $^3J_{H(13)H(14)}$ = 7.8 Hz), 7.19 (br.dd, H(12), $^3J_{H(11)H(12)}$ = 8.1 Hz, $^3J_{H(13)H(12)}$ = 7.5 Hz); 7.38 (br.ddm, H(13), $^3J_{H(14)H(13)}$ = 7.8 Hz, $^3J_{H(12)H(13)}$ = 7.5 Hz, $^4J_{H(11)H(13)}$ = 1.4 Hz); 7.55 (br.d, H(11), $^3J_{H(11)H(12)}$ = 8.1 Hz); 7.50 (m, H(17)); 7.56 (m, H(18)); 8.04 (br.ddm, H(16), $^3J_{PCCH(16)}$ = 16.0 Hz, $^3J_{H(17)H(16)}$ = 8.4 Hz, $^4J_{H(18)H(16)}$ = 1.2 Hz). ^{19}F NMR ($CDCl_3$), δ: –72.81 (q, CF_3, $^4J_{FF}$ = 10.7 Hz); –73.86 (q, CF_3, $^4J_{FF}$ = 10.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 101.92 (ddq [dq], C(3), $^1J_{HC(3)}$ = 190.6 Hz, $^2J_{POC(3)}$ = 6.6 Hz, $^5J_{FCCCOC(3)}$ = 2.8 Hz); 88.62 (br.dd [d], C(5), $^1J_{PC(5)}$ = 109.9 Hz, $^3J_{HC(11)CC(5)}$ = 3.5 Hz); 125.10 (m [d], C(6), $^2J_{PCC(6)}$ = 5.7 Hz); 153.83 (br.dddd [d], C(7), $^2J_{POC(7)}$ = = 8.8—9.0 Hz, $^3J_{HC(11)CC(7)}$ = 8.8—9.0 Hz, $^3J_{HC(13)CC(7)}$ = = 8.8—9.0 Hz, $^2J_{HC(14)C(7)}$ = 3.3 Hz); 80.49 (septd [septd], C(10), $^2J_{FCC(10)}$ = 30.6 Hz, $^2J_{PCC(10)}$ = 13.8 Hz); 127.75 (br.ddd [d], C(11), $^1J_{HC(11)}$ = 162.7 Hz, $^3J_{PCCC(11)}$ = 18.2 Hz, $^3J_{HC(13)CC(11)}$ = = 8.6 Hz); 124.43 (dd [s], C(12), $^1J_{HC(12)}$ = 162.1 Hz, $^3J_{HC(14)CC(12)}$ = 7.8 Hz); 131.71 (ddd [s], C(13), $^1J_{HC(13)}$ = = 160.7 Hz, $^3J_{HC(11)CC(13)}$ = 8.6 Hz, $^2J_{HCC(13)}$ = 1.6—1.7 Hz); 112.96 (ddd [d], C(14), $^1J_{HC(14)}$ = 164.9 Hz, $^3J_{POCC(14)}$ = 12.8 Hz, $^3J_{HC(12)CC(14)}$ = 8.2—8.3 Hz); 135.25 (dt [d], C(15), $^1J_{PC(15)}$ = = 235.5 Hz, $^3J_{HC(17),C(19)CC(15)}$ = 7.8 Hz); 131.17 (br.dddd [d], C(16), C(20), $^1J_{HC(16),C(20)}$ = 162.7 Hz, $^2J_{PCC(16),C(20)}$ = 11.0 Hz, $^3J_{HC(18)CC(16)}$ = 7.4 Hz, $^3J_{HC(20)CC(16)}$ = 7.4 Hz); 128.28 (ddd [d], C(17), C(19), $^1J_{HC(17),C(19)}$ = 161.6 Hz, $^3J_{PCCC(17),C(19)}$ = 18.3 Hz, $^3J_{HC(19)CC(17)}$ = 7.5 Hz); 131.37 (dtd [d], C(18), $^1J_{HC(18)}$ = 160.2 Hz, $^3J_{HC(16),C(20)CC(18)}$ = 7.5 Hz, $^4J_{PCCCC(18)}$ = 3.6 Hz); 97.57 (dd [d], C(21), $^2J_{HC(3)C(21)}$ = 11.4 Hz, $^3J_{POCC(21)}$ = 3.5 Hz); 120.95 (qd [qd], C(22), $^1J_{FC(22)}$ = 285.1 Hz, $^3J_{POCC(22)}$ = 12.8 Hz); 121.01 (qd [qd], C(23), $^1J_{FC(23)}$ = 285.1 Hz, $^3J_{POCC(23)}$ = 8.0 Hz).

Phosphorane **6** (3.25 g, 0.006 mol) in contact with atmospheric moisture under mild conditions (air exposure in $CDCl_3$ (7 mL) at 20 °C) underwent hydrolysis into **2-oxo-2-phenyl-5-(2,2,2-trichloro-1-hydroxyethoxy)-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,2λ^5-benzodioxaphosphepine (7).** Yield 1.61 g (48%), colorless crystals, m.p. 152 °C. Found (%): C, 38.49; H, 2.33; P, 5.47. $C_{18}H_{12}Cl_3F_6O_5P$. Calculated (%): C, 38.61; H, 2.14; P, 5.54. ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$ + DMSO-d_6 (20%)), δ_P: 6.5 (s). ^{1}H NMR (600 MHz, $CDCl_3$ + DMSO-d_6 (20%)), δ: 5.27 (s, H(5)); 6.23 (s, H(16)); 6.82 (d, H(9), $^3J_{H(8)H(9)}$ = = 7.5 Hz); 7.33 (m, H(12)); 7.50 (m, H(11)); 7.54 (m, H(13)); 7.56 (br.dd, H(7), $^3J_{H(8)H(7)}$ = 7.7 Hz, $^3J_{H(6)H(7)}$ = 7.6 Hz); 7.67 (br.dd, H(8), $^3J_{H(7)H(8)}$ = 7.7 Hz, $^3J_{H(9)H(8)}$ = 7.5 Hz); 7.82 (br.dd, H(6), $^3J_{H(7)H(6)}$ = 7.6 Hz, $^4J_{H(8)H(6)}$ = 1.2—1.4 Hz); 8.63 (br.s, OH). ^{13}C NMR ($CDCl_3$ + DMSO-d_6 (20%)), δ: 79.85 (septm [septd], C(4), $^2J_{FCC(4)}$ = 31.2 Hz, $^2J_{POC(4)}$ = 7.5—8.5 Hz); 67.83 (br.d [br.s], C(5), $^1J_{HC(5)}$ = 146.6 Hz); 125.44 (m [s],

C(5a)); 127.59 (br.dd [br.s], C(6), $^1J_{HC(6)}$ = 165.2 Hz, $^3J_{HC(8)CC(6)}$ = 7.5 Hz, $^3J_{HC(5)CC(6)}$ = 3.5—4.0 Hz); 124.19 (dd [s], C(7), $^1J_{HC(7)}$ = 162.8 Hz, $^3J_{HC(9)CC(7)}$ = 7.8 Hz); 128.95 (dd [s], C(8), $^1J_{HC(8)}$ = 162.8 Hz, $^3J_{HC(6)CC(8)}$ = 9.0 Hz); 117.96 (br.dm [d], C(9), $^1J_{HC(9)}$ = 165.2 Hz, $^3J_{HC(6)CC(8)}$ = 8.4 Hz, $^3J_{POCC(9)}$ = = 4.8 Hz); 145.23 (m [d], C(9a), $^2J_{POC(9a)}$ = 9.0 Hz); 123.00 (dt [d], C(10), $^1J_{PC(10)}$ = 199.4 Hz, $^3J_{HC(12)CC(10)}$ = 7.8 Hz); 127.27 (dddd [d], C(11), C(15), $^1J_{HC(11)}$ = 164.6 Hz, $^2J_{PCC(11)}$ = = 10.2 Hz, $^3J_{HC(11)CC(11)}$ = 7.3 Hz, $^3J_{HC(13)CC(11)}$ = 7.3 Hz); 127.27 (dddd [d], C(12), $^1J_{HC(12)}$ = 163.4 Hz, $^3J_{PCCC(12)}$ = 16.8 Hz, $^3J_{HC(12)CC(12)}$ = 7.0 Hz, $^2J_{HCC(12)}$ = 1.6 Hz); 132.48 (br.dm [br.d], C(13), $^1J_{HC(13)}$ = 161.0 Hz, $^3J_{HC(11)CC(13)}$ = 7.4 Hz, $^4J_{PCCCC(13)}$ = 3.5 Hz); 119.53 (qd [br.q], C(14), $^1J_{FC(14)}$ = 290.2 Hz, $^3J_{HC(5)CC(14)}$ = 3.0 Hz); 119.33 (qdd [qd], C(15), $^1J_{FC(15)}$ = = 289.6 Hz, $^3J_{POCC(15)}$ = 10.2 Hz, $^3J_{HC(5)CC(15)}$ = 9.0 Hz); 98.62 (dd [s], C(16), $^1J_{HC(16)}$ = 172.4 Hz, $^3J_{HC(5)OC(16)}$ = 5.1 Hz); 97.78 (d [s], C(17), $^2J_{HC(16)C(17)}$ = 6.0 Hz).

Table 3. Crystallographic parameters and the data collection statistics for structures **5** and **6**

Parameter	**5**	**6**
Color	Colorless	
Crystal shape	Prisms	
Molecular formula	$C_{16}H_{11}F_6O_4P$	$C_{18}H_{10}Cl_3F_6O_4P$
Molecular weight	412.22	541.58
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	10.675(2)	8.731(8)
b/Å	12.242(2)	10.04(2)
c/Å	13.459(2)	12.282(8)
α/deg	—	93.52(2)
β/deg	110.18(1)	95.24(3)
γ/deg	—	103.54(3)
V/Å^3	1650.9(5)	1039(2)
Z	4	2
d_{calc}/g cm^{-3}	1.658	1.732
Absorbance, μ(Cu)/cm^{-1}	23.09	54.75
Absorption correction	Psi-scan	
Radiation (λ/Å)	Cu-Kα (1.54184)	
F(000)	832	540
Number of measured reflections	3515	5283
R_{int}	0.0546	0.4918
Number of independent reflections with $I > 2\sigma(I)$	3364	3899
Discrepancy factors ($I > 2\sigma(I)$)		
R	0.0678	0.1219
R_w	0.1921	0.2829
GOOF	1.120	0.961
Number of parameters refined	253	289
Ranges of h, k, l indices	$-13 \le h \le 12$, $0 \le k \le 15$, $0 \le l \le 16$	$-10 \le h \le 10$, $-5 \le k \le 12$, $-15 \le l \le 15$
Residual electron density/e·Å^{-3}, ρ_{max}/ρ_{min}	0.442/−0.401	0.350/−0.322

Single-crystal X-ray diffraction study of compounds **5** and **6** was performed at the X-ray Diffraction Division of the Collective Use Center of the Spectroanalytical Center based on the Diffraction Investigations Laboratory of the A. E. Arbuzov Institute of Organic and Physical Chemistry (Kazan Research Center, Russian Academy of Sciences). The crystallographic parameters and the data collection and refinement statistics for structures **5** and **6** are given in Table 3. The experiments were carried out on a Nonius B.V. CAD-4 automatic four-circle diffractometer at −150 (**5**) and 20 °C (**6**) (graphite monochromator, λ(Cu-Kα) radiation). The collected data were first processed with the MolEN program[25] on an AlphaStation 200 computer. The intensities of three check reflections showed no decay during the data collection; absorption correction was applied empirically. All structures were solved by the direct methods with the SIR program[26] and refined first isotropically and then anisotropically with the SHELXL-97 (see Ref. 27) and WinGX programs.[28] The H atoms of the hydroxy groups in structure **5** were located from difference electron-density maps; the positions of the other H atoms in both the structures were calculated from stereochemical considerations and refined using appropriate riding models. Intermolecular interactions were analyzed, and figures were drawn, with the PLATON program.[29]

The atomic coordinates and thermal parameters for structures **5** and **6** have been deposited with the Cambridge Crystallographic Data Center (http://www.ccdc.cam.ac.uk; CCDC Nos. 710 244 and 710 245, respectively).

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