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# Synthesis, crystal structure and hydrolysis of novel isomeric cage ( $\mathrm{P}-\mathrm{C} / \mathrm{P}-\mathrm{O}$ )-phosphoranes on the basis of 4,4,5,5-tetramethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane and hexafluoroacetone $\dagger$ 

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#### Abstract

The reaction of 4,4,5,5-tetramethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane with hexafluoro acetone leads to the simultaneous formation of regioisomeric cage ( $\mathrm{P}-\mathrm{C} / \mathrm{P}-\mathrm{O}$ )-phosphoranes, the structures of which are unequivocally confirmed by XRD. The rearrangement of the $\mathrm{P}-\mathrm{C}$-isomer to $\mathrm{P}-\mathrm{O}-$ isomer with high stereoselectivity ( $>96 \%$ ) takes place in methylene chloride solution with the retention of the phosphorus coordination. It was found that the stepwise hydrolysis of the P - O -isomer initially gives 2-(2,3-dihydroxy-1,2-diphenyl-3-trifluoromethyl-4,4,4-trifluorobutyloxy)-4,4,5,5-tetramethyl-2-oxo-1,3,2dioxaphospholane as the only stereoisomer whose structure is also confirmed by XRD. Further hydrolysis of this compound leads to the formation of 2,3-dihydroxy-3-trifluoromethyl-4,4,4-trifluoro-1,2diphenylbutylphosphate and pinacol, which forms the solvate in the crystal. Hydrolysis of the P-C-isomer yields 2-hydroxy-4,4,5,5-tetramethyl-2-oxo-1,3,2-dioxaphospholane, benzoin and hexafluoroisopropanol.


## Introduction

Pentacoordinated phosphorus compounds are key intermediates in phosphoryl group transfer reactions, which are important in the processes of cell viability ${ }^{1-7}$ and in the origin and development of life. ${ }^{8}$ Such phosphorus derivatives are intermediates in the nucleophilic substitution reactions at the tetrahedral phosphorus atom, ${ }^{9-13}$ among which the most important for organic synthesis are the Wittig, ${ }^{14}$ Appel,,${ }^{15,16}$ and Mitsunobu ${ }^{17-19}$ reactions, which are well described. Therefore, the synthesis, structure and chemical transformations of phosphoranes have attracted considerable attention. ${ }^{20-27}$ Among the diverse synthetic methods for the preparation of phosphoranes, several general approaches based on the addition reactions of P (iiI)-derivatives to unsaturated systems, various reactions of tetracoordinated phosphorus and substitution reactions at $\mathrm{P}(\mathrm{v})^{28,29}$ should be noted.

[^0]Recently, we developed a new approach for the preparation of phosphoranes based on the cascade reactions of $\mathrm{P}(\mathrm{III})$-derivatives, containing an unsaturated moiety with carbonyl compounds, which leads to $\mathrm{P}(\mathrm{v})-\mathrm{C}$ cage heterocycles. ${ }^{30-34}$ Scheme 1, which shows the synthetic possibilities of this approach, is an example of the reactions of benzodioxaphosphole derivatives 1 with hexafluoroacetone. It is assumed that the reactions proceed through intermediate $\mathrm{P}^{+}-\mathrm{C}-\mathrm{O}^{-}$bipolar ions followed by the transfer of the reactive center on the exocyclic unsaturated substituent, which lead to the formation of the corresponding cage phosphoranes 24 bearing the $\mathrm{P}-\mathrm{C}$-bond. ${ }^{30-32}$

Scheme 2 demonstrates the synthetic potential of the intramolecular cascade cyclization of $\mathrm{P}(\mathrm{III})$-derivatives 1 under the


Scheme 1 Use of $\mathrm{P}($ (II)-derivatives bearing an exocyclic $\mathrm{C}=\mathrm{O}$ or $\mathrm{C}=\mathrm{N}$ bond in the synthesis of cage phosphoranes.


Scheme 2 Reaction of $\mathrm{P}($ II)-derivatives 1 bearing an exocyclic $\mathrm{C}=\mathrm{O}$ bond with trifluoropyruvic acid ethyl ester and chloral.


Scheme 3 Simultaneous formation of PCO- and POC-isomers 10 and 11 in the reaction of phospholane 1 with hexafluoroacetone.
action of prochiral trifluoropyruvic acid ethyl ester and chloral, which allows the P-C-cage phosphoranes 5-8 to be obtained with high stereoselectivity. ${ }^{33,34}$

None of these reactions afford pentaalkoxyphosphoranes, the products of intramolecular PCO/POC-rearrangement, which is characteristic to the reaction of ordinary trialkylphosphites with the carbonyl compounds mentioned above. ${ }^{35,36}$

Recently, we have shown ${ }^{37}$ that the inclusion of a phosphorus(III) atom in the dioxaphospholane cycle results in the simultaneous formation of PCO- and POC-isomers $(1: 1)$ of cage phosphoranes ${ }^{10,11}$ in the reaction of 4,5-dimethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane ${ }^{9}$ with hexafluoro acetone (Scheme 3). PCO-phosphorane $\mathbf{1 0}$ is subjected to intramolecular PCO/POC-rearrangement during storage $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, 20^{\circ} \mathrm{C}, 30\right.$ days) and yields the POC-species 11.

## Results and discussion

Considering that the related PCO/POC-rearrangement in a series of 1-hydroxyalkylphosphonates (-phosphinates) is facilitated not only by electron-withdrawing substituents at the carbon atom bonded with OH -group, but also electron-donor substituents at the phosphorus atom, ${ }^{38}$ we introduced $4,4,5,5$-tetramethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane 12 in the reaction with hexafluoroacetone. Tetramethyl-substituted dioxaphospholane 12 has essentially more electron donor cyclic moieties as compared with the dimethyl-substituted phospholane 9 , which, however, also effectively stabilizes the phosphorus pentacoordinated state. Compound 12 was obtained by the phosphorylation of benzoin with 2 -chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in the presence of triethylamine according to the data. ${ }^{39}$

The reaction of phosphite 12 with hexafluoroacetone proceeds in mild conditions $\left(\mathrm{CCl}_{4},-40{ }^{\circ} \mathrm{C}\right)$ with the simultaneous formation of two isomeric pentacoordinated phosphorus
species 13 and 14 (Scheme 4), which have two high-field signals at $\delta_{\mathrm{P}}-24.5$ and $\delta_{\mathrm{P}}-26.5 \mathrm{ppm}$ in a ratio of $10: 1$ in their ${ }^{31} \mathrm{P}-$ $\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (a day after the reaction). The molecular ion peaks for compounds 13 and 14 are identical (ESI, m/z 523.9) and correspond to the reaction products with a composition of $1: 1$, and their fragmentation is not significantly different. After the removal of the solvent, the oily residue crystallizes with the formation of compound $\mathbf{1 3}$ during storage. It manifests itself as a doublet in the high-field region $\left(\mathrm{CCl}_{4}, \delta_{\mathrm{P}}-25.1 \mathrm{ppm},{ }^{3} J_{\mathrm{PCCH}}=\right.$ 15.6 Hz) of the ${ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum. Taking into account the spectral data (see ESI $\dagger$ ), we determined the structure of compound 13 to be 1-(2,3-butylenedioxy)-6,6-bis (trifluoromethyl)-3,4-diphenyl-1,2,5,7-phosphatrioxabicyclo [2.2.1 ${ }^{1,4}$ ]heptane. The ${ }^{19} \mathrm{~F}$ NMR spectrum contains two signals at $\delta_{\mathrm{F}}-68.48\left(\mathrm{qd},{ }^{4} J_{\mathrm{FCCCF}}=10.3 \mathrm{~Hz},{ }^{3} J_{\mathrm{PCCF}}=4.6 \mathrm{~Hz}\right)$ and $\delta_{\mathrm{F}}-68.94$ $\operatorname{ppm}\left(q d,{ }^{4} J_{\text {FCCCF }}=10.3 \mathrm{~Hz},{ }^{3} J_{\mathrm{PCCF}} 2.3 \mathrm{~Hz}\right)$ with an equal integral intensity, which correspond to the non-equivalent fluorine atoms of $\mathrm{CF}_{3}$-groups. In contrast to the abovementioned phosphite 9 , which is a hexafluoroacetone system, the formation of PC-phosphorane $\mathbf{1 3}$ is a kinetically preferred process.

The structure of phosphorane 13 was confirmed by single crystal XRD. The geometry of molecule 13 in the crystal (conglomerate) is shown in Fig. 1, and the main geometrical parameters (bond lengths and bond and torsion angles) are listed in the figure caption. The configuration of the chiral atoms is $\mathrm{P}_{R}{ }^{1} \mathrm{C}_{R}{ }^{3} \mathrm{C}_{S}{ }^{4}$. A small deviation in the phosphorus atom from the $\mathrm{O}^{3} \mathrm{O}^{2} \mathrm{O}^{6}$ plane [by $-0.114(2) \AA$ A allows us to conclude that the phosphorus atom has a slightly distorted trigonal bipyramidal configuration with a planar 0.085(2) A base, formed by the $\mathrm{P}^{1}, \mathrm{O}^{2}, \mathrm{O}^{3}$ and $\mathrm{C}^{6}$ atoms. The $\mathrm{O}^{1}$ and $\mathrm{O}^{7}$ atoms located in the apical positions deviate from this plane by -1.696 (5) and $1.619(5) \AA$, respectively [bond angle of $\hat{\mathrm{I}}^{1}-\mathrm{P}^{1}-\mathrm{O}^{7}$ is equal to 172.4




16
17

Scheme 4 The reaction of phospholane 12 with hexafluoroacetone. The same numbering of the atoms in structures 13-17 is given for convenience.


Fig. 1 Geometry of molecule 13 in a crystal (conglomerate). Selected bond lengths ( $\AA$ ), and bond and torsion angles ( ${ }^{\circ}$ ): $\mathrm{P}^{1}-\mathrm{O}^{1} 1.613(5), \mathrm{P}^{1}-$ $O^{2} 1.619(5), P^{1}-O^{3} 1.583(5), P^{1}-O^{7} 1.711(5), P^{1}-C^{6} 1.930(7), O^{1}-P^{1}-O^{2}$ 96.3(3), $O^{1}-P^{1}-O^{3} 92.7(3), O^{1}-P^{1}-O^{7} 172.4(3), O^{1}-P^{1}-C^{6} 92.8(3), O^{2}-$ $P^{1}-O^{3} 120.9(3), O^{2}-P^{1}-O^{7} 90.3(2), O^{2}-P^{1}-C^{6} 100.7(3), O^{3}-P^{1}-O^{7}$ 85.7(2), $\quad O^{3}-P^{1}-C^{6}$ 136.9(3), $O^{7}-P^{1}-C^{6}$ 83.3(3), $C^{9}-C^{7}-C^{8}-C^{12}$ $-161.4(8), P^{1}-O^{7}-C^{4}-C^{19} 177.5(5), C^{13}-C^{3}-C^{4}-C^{19} 46.2(8)$ and $O^{7}-$ $C^{4}-C^{19}-C^{20} 1(1)$. Hereinafter, non-hydrogen atoms are shown in view of thermal ellipsoids with a probability of $30 \%$, and the trigonal pyramid base is outlined with thin lines.
$\left.\left(3^{\circ}\right)\right]$. One of the two trifluoromethyl groups $\left(\mathrm{C}^{25} \mathrm{~F}_{3}\right)$ is almost in this plane [ $\mathrm{C}^{25}$ atom deviation from it is $0.21(1) \AA$ ]. The $\mathrm{O}^{1}-\mathrm{P}^{1}-$ $\mathrm{O}^{3}, \mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{2}, \mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{C}^{6}, \mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{7}, \mathrm{O}^{7}-\mathrm{P}^{1}-\mathrm{C}^{6}$ and $\mathrm{O}^{3}-\mathrm{P}^{1}-\mathrm{O}^{7}$ bond angles vary within the limits of 83.3(3)-96.9(3) ${ }^{\circ}$. The $\mathrm{O}^{2}-$ $\mathrm{P}^{1}-\mathrm{C}^{6}, \mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{3}$ and $\mathrm{O}^{3}-\mathrm{P}^{1}-\mathrm{C}^{6}$ bond angle sum in the pyramid base is equal to $358.5(2)^{\circ}$ and points to a trigonal bipyramidal phosphorus configuration close to an almost regular configuration. The $\mathrm{P}^{1}-\mathrm{O}^{3}$ equatorial bond length is slightly smaller [1.583(5) $\AA$ ] than the $\mathrm{P}^{1}-\mathrm{O}^{1}$ and $\mathrm{P}^{1}-\mathrm{O}^{7}$ axial bond lengths of [1.613(3) and 1.711(5) $\AA$ ].

The concurrence of the $\mathrm{P}^{1}-\mathrm{O}^{1}$ and $\mathrm{P}^{1}-\mathrm{O}^{7}$ axial bond length sum $[3.324(5) \AA]$ and $\mathrm{O}^{1} \cdots \mathrm{O}^{7}$ distance $[3.317(7) \AA]$ can be considered as evidence of the regular trigonal bipyramidal phosphorus configuration. The $\mathrm{P}^{1}-\mathrm{C}^{6}$ bond length is equal to 1.930 (7) A. A five-membered dioxaphospholane cycle occupies the axial-equatorial position in the trigonal bipyramid ( $\mathrm{O}^{1}$ is axial and $\mathrm{O}^{3}$ is equatorial), its conformation is envelope, where four atoms, $\mathrm{O}^{1}, \mathrm{P}^{1}, \mathrm{O}^{3}$ and $\mathrm{C}^{8}$, lie in one plane [planar within $0.004(5) \AA]$, and the $\mathrm{C}^{7}$ atom deviates from this plane by $0.518(9)$ $\AA$. The $\mathrm{C}^{9}$ and $\mathrm{C}^{12}$ atoms deviate from this plane by $2.05(1)$ and $-1.43(1) \AA$, respectively, and they occupy axial positions in the cycle. The $\mathrm{C}^{10}$ and $\mathrm{C}^{11}$ atoms also deviate from the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{8}$ plane by $-0.05(1)$ and $0.91(1) \AA$, respectively, and are located in equatorial positions. The $\mathrm{O}^{2}$ and $\mathrm{C}^{6}$ atoms deviate in opposite sides from the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{7}$ plane [their deviations are $1.377(5)$ and $-1.297(8) \AA$, respectively] and occupy equatorial and axial positions in the five-membered cycle. The $\mathrm{C}^{10}$ and $\mathrm{O}^{7}$ deviations are minimal [they deviate by $-0.05(1)$ and $-0.213(5) \AA$, respectively] and we can assume that they lie in the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{8}$ plane.

The $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{8}$ fragment can also be considered as a part of the most elongated seven-membered approximately planar $\mathrm{C}^{8} \mathrm{O}^{3} \mathrm{P}^{1} \mathrm{O}^{1} \mathrm{O}^{7} \mathrm{C}^{4} \mathrm{C}^{19}$ system [planar within $0.135(5) \AA$ ]. The plane of the phenyl substituent in the fourth position of the bicycloheptane $\mathbf{1 3}$ is slightly turned in the dihedral angle of $6.2(5)^{\circ}$ relative to the seven-membered fragment. The conformation of the five-membered $\mathrm{P}^{1} \mathrm{O}^{2} \mathrm{C}^{3} \mathrm{C}^{4} \mathrm{O}^{7}$ cycle of molecule 13 is envelope (Fig. 1). It includes a four-membered plane $\mathrm{P}^{1} \mathrm{O}^{2} \mathrm{C}^{3} \mathrm{C}^{4}$ fragment [planar within $0.025(5) \AA$ ], and the $\mathrm{O}^{7}$ atom deviates from this plane by $0.760(5) \AA$. The $\mathrm{O}^{1}, \mathrm{O}^{3}, \mathrm{O}^{5}, \mathrm{C}^{6}, \mathrm{C}^{13}$ and $\mathrm{C}^{19}$ atoms deviate from the abovementioned fragment by the values of $-0.742(5), 1.302(5),-1.391(5),-1.574(7), 1.257(7)$ and $0.355(3)$ $\AA$, respectively. This is due to fact that the $\mathrm{C}^{13}$ and $\mathrm{C}^{19}$ atoms deviate to one side point out of the cis-orientation of the phenyl substituents in the five-membered cycle discussed above. The conformation of the other five-membered $\mathrm{P}^{1} \mathrm{C}^{6} \mathrm{O}^{5} \mathrm{C}^{4} \mathrm{O}^{7}$ ring of the rigid bicycloheptane scaffold is a slightly distorted envelope. The four-membered $\mathrm{P}^{1} \mathrm{C}^{6} \mathrm{O}^{5} \mathrm{C}^{4}$ fragment is planar within $0.066(5) \AA$, and the $\mathrm{O}^{7}$ atom deviates from this plane by $-0.853(5) \AA$. The $\mathrm{O}^{1}, \mathrm{O}^{2}, \mathrm{O}^{3}, \mathrm{C}^{3}, \mathrm{C}^{19}, \mathrm{C}^{25}$ and $\mathrm{C}^{26}$ atoms deviate from the abovementioned fragment by the values of $-0.699(5)$, $1.392(5),-0.949(5), 1.337(7),-0.579(7),-1.40(1)$ and 1.097(9) A., respectively.

During storage in very polar dichloromethane at $20^{\circ} \mathrm{C}$ for about five days, compound $\mathbf{1 3}$ underwent a gradual conversion to compound 14 (after four days, the ratio of compounds $\mathbf{1 3} / \mathbf{1 4}$ was 1 to 20). Fig. 2 shows the spectral image of this process according to ${ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR. The figure shows that phosphorane $13\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, \delta_{\mathrm{P}}-25.0 \mathrm{ppm}\right)$ was completely converted to pentaoxyphosphorane $14\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, \delta_{\mathrm{P}}-26.7 \mathrm{ppm}\right)$, which is a minor compound in the reaction in tetrachloromethane. This compound was isolated in the individual state by crystallization under a layer of pentane and characterized by spectral methods, which allowed the assignment of the structure of 1-(2,3-butyle-nedioxy)-5,5-bis(trifluoromethyl)-3,4-diphenyl-1,2,6,7-phosphatrioxabicyclo[2.2.1 ${ }^{1,4}$ ]heptane 14, the product of PCO/POCrearrangement. In the ${ }^{13} \mathrm{C}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound 14, the carbon atom bonded to $\mathrm{CF}_{3}$-groups resonates at 83.41 ppm as a septet with coupling through two bonds from fluorine $\left({ }^{2} J_{\mathrm{CCF}}=29.3 \mathrm{~Hz}\right)$, unlike the spectrum of compound 13 in which the oxygenated carbon in the $\mathrm{OC}\left(\mathrm{CF}_{3}\right)_{2}$ fragment manifests itself as a doublet of septets at 77.78 ppm with direct spin-spin coupling from phosphorus ( ${ }^{1} J_{\mathrm{PC}}=154.8 \mathrm{~Hz},{ }^{2} J_{\mathrm{FCC}}=30.7 \mathrm{~Hz}$ ). The signals of the $\mathrm{CF}_{3}$-groups in the ${ }^{19} \mathrm{~F}$ NMR spectrum of compound 14 appear as two quartets at $\delta_{\mathrm{F}}-68.22 \mathrm{ppm}$ and $-72.35 \mathrm{ppm}\left({ }^{4} J_{\mathrm{FCCCF}}=9.5 \mathrm{~Hz}\right)$.

Its structure was also confirmed by single crystal XRD. Fig. 3 presents the geometry of the molecule in a crystal (the main geometrical parameters, including bond length, valence and torsion angles of the molecule above, are presented in the ESI file $\dagger$ ). The configuration of the chiral atoms is $\mathrm{P}_{R}{ }^{1} \mathrm{C}_{R}{ }^{3} \mathrm{C}_{S}{ }^{4} / \mathrm{P}_{S}{ }^{1-}$ $\mathrm{C}_{S}{ }^{3} \mathrm{C}_{R}{ }^{4}$ (racemate). The meaningless deviation of the phosphorus atom from the $\mathrm{O}^{3} \mathrm{O}^{2} \mathrm{C}^{6}$ plane by $-0.0580(7) \AA$ allows to conclude that the geometry of phosphorus in molecule $\mathbf{1 4}$ is a slightly distorted trigonal bipyramid with a planar base [within $0.043(2) \AA$ A ], where the $\mathrm{P}^{1}, \mathrm{O}^{2}, \mathrm{O}^{3}, \mathrm{C}^{6}$ atoms are located. The $\mathrm{O}^{1}$ and $\mathrm{O}^{7}$ atoms located in apical positions deviate from


Fig. 2 Conversion of $\mathrm{P}-\mathrm{C}$-phosphorane 13 to P -O-species 14 according to ${ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$, in one day, and after two, three and five days).


Fig. 3 Geometry of molecule 14 in a crystal (racemate, $\mathrm{P}_{S}{ }^{1} \mathrm{C}_{S}{ }^{3} \mathrm{C}_{R}{ }^{4}$ enantiomer is shown). The base of the trigonal bipyramid is shown by thin lines. Selected bond lengths ( $\AA$ ) and bond and torsion angles ( ${ }^{\circ}$ ): $P^{1}-O^{1} 1.625(2), P^{1}-O^{2} 1.606(2), P^{1}-O^{3} 1.582(2), P^{1}-O^{6} 1.647(2), P^{1}-O^{7}$ $1.700(2), \mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{2} 92.1(1), \mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{3} 92.4(1), \mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{7} 177.5(1), \mathrm{O}^{1}-$ $\mathrm{P}^{1}-\mathrm{O}^{6} 91.6(1), \mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{3}$ 126.4(1), $\mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{7} 90.4(1), \mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{6}$ 105.8(1), $\mathrm{O}^{3}-\mathrm{P}^{1}-\mathrm{O}^{7} 86.1(1), \mathrm{O}^{3}-\mathrm{P}^{1}-\mathrm{O}^{6}$ 127.4(1), $\mathrm{O}^{6}-\mathrm{P}^{1}-\mathrm{O}^{7} 87.8(1)$, $C^{9}-C^{7}-C^{8}-C^{11}-164.4(4), P^{1}-O^{7}-C^{4}-C^{19} 178.8(2), C^{13}-C^{3}-C^{4}-C^{19}$ -40.9 (3) and $\mathrm{O}^{7}-\mathrm{C}^{4}-\mathrm{C}^{19}-\mathrm{C}^{20} 10.0(4)$.
the above plane by the values of $-1.625(2)$ and $1.700(2) \AA$ [the valence angle of $\mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{7}$ is equal to $\left.177.5(1)^{\circ}\right]$. The values of the valence angles $\mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{3}, \mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{2}, \mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{6}, \mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{7}$, $\mathrm{O}^{6}-\mathrm{P}^{1}-\mathrm{O}^{7}$ and $\mathrm{O}^{3}-\mathrm{P}^{1}-\mathrm{O}^{7}$ vary within the limits of $86.1(1)-$ $92.4(1)^{\circ}$, and the sum of the valence angles of $\mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{6}, \mathrm{O}^{2}-\mathrm{P}^{1}-$ $\mathrm{O}^{3}$ and $\mathrm{O}^{3}-\mathrm{P}^{1}-\mathrm{O}^{6}$ at the pyramid base is $359.6(2)^{\circ}$, which also indicate the trigonal-bipyramidal configuration of the phosphorus atom close to the regular configuration. The equatorial $\mathrm{P}^{1}-\mathrm{O}^{2}, \mathrm{P}^{1}-\mathrm{O}^{3}$ and $\mathrm{P}^{1}-\mathrm{O}^{6}$ bonds [1.606(2), 1.582(2), and 1.647(2) $\AA$, respectively] are slightly shorter than the axial $\mathrm{P}^{1}-\mathrm{O}^{1}$ and $\mathrm{P}^{1}-$ $\mathrm{O}^{7}$ bonds [1.625(2) and $1.700(2) \AA$, respectively]. The fact of practical coincidence of the $\mathrm{P}^{1}-\mathrm{O}^{1}$ and $\mathrm{P}^{1}-\mathrm{O}^{7}$ axial bond values sum $\left[3.325(5) \AA\right.$ ] and $\mathrm{O}^{1} \cdots \mathrm{O}^{7}$ distance $[3.323(7) \AA$ i $]$ is in favor of the regular trigonal bipyramid configuration. The fivemembered tetramethyldioxaphospholane cycle occupies the axial-equatorial position in the trigonal bipyramid ( $\mathrm{O}^{1}$ atom is axial and $\mathrm{O}^{3}$ atom is equatorial). Its conformation is a distorted envelope, where four $\mathrm{O}^{1}, \mathrm{P}^{1}, \mathrm{O}^{3}$ and $\mathrm{C}^{7}$ atoms lie in one plane [planar within $0.0482(7) \AA$ ], and the $\mathrm{C}^{8}$ atom deviates from the above plane by $0.422(4) \AA$. The $C^{9}$ and $C^{12}$ atoms deviate from the plane to the opposite sides by the rather significant distances of $-1.525(5)$ and $1.963(6) \AA$, respectively (they occupy axial positions in the cycle), and the $\mathrm{C}^{10}$ and $\mathrm{C}^{11}$ atoms also deviate by the different values of $0.758(5)$ and $-0.178(6) \AA$ (they occupy equatorial positions in the cycle). The $\mathrm{O}^{2}$ and $\mathrm{O}^{6}$ atoms deviate to opposite sides from the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{7}$ plane and occupy equatorial and axial positions in the five-membered cycle [their deviations are $1.182(2)$ and $-1.406(2) \AA$, respectively]. The $\mathrm{O}^{7}$ atom deviation is minimal $[-0.213(5) \AA]$; thus, it can be concluded that this atom lies in the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{7}$ plane. Moreover, it should be noticed that the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{7}$ fragment is turned to be a part of the more extended planar moiety of $\mathrm{C}^{7} \mathrm{O}^{3} \mathrm{P}^{1} \mathrm{O}^{1} \mathrm{O}^{3} \mathrm{O}^{7} \mathrm{C}^{4} \mathrm{C}^{19}$ in the molecule [planar within $0.054(4) \AA$ A . The plane of the phenyl substituent position $4\left(\mathrm{C}^{19-24}\right)$ is slightly turned to this seven-membered fragment [the dihedral angle between the corresponding planes is larger than the angle in molecule 13 and is equal to $\left.9.2(2)^{\circ}\right]$. The conformation of the five-membered $\mathrm{P}^{1} \mathrm{O}^{2} \mathrm{C}^{3} \mathrm{C}^{4} \mathrm{O}^{7}$ cycle of the rigid bicycloheptane system of molecule $\mathbf{1 4}$ is an envelope [it contains a planar fourmembered $\mathrm{P}^{1} \mathrm{O}^{2} \mathrm{C}^{3} \mathrm{C}^{4}$ fragment within $0.033(2) \AA$, and the $\mathrm{O}^{7}$ atom deviates from it by $0.806(2) \AA$ A]. The $\hat{\mathrm{I}}^{1}, \mathrm{O}^{3}, \mathrm{C}^{5}, \mathrm{O}^{6}, \mathrm{C}^{13}$ and $\mathrm{C}^{19}$ atoms deviate from the abovementioned planar fragment by values of $-0.726(2), 1.224(2),-1.428(3),-1.341(2), 1.276(3)$ and $0.485(3) \AA$, respectively. The fact that the $\mathrm{C}^{13}$ and $\mathrm{C}^{19}$ atoms deviate to one side suggests the cis-orientation of the phenyl substituents in the abovementioned five-membered cycle. The conformation of the other five-membered $\mathrm{P}^{1} \mathrm{O}^{6} \mathrm{C}^{5} \mathrm{C}^{4} \mathrm{O}^{7}$ cycle of the rigid bicycloheptane system of molecule 14 is a slightly distorted envelope [four-membered $\mathrm{P}^{1} \mathrm{O}^{6} \mathrm{C}^{5} \mathrm{C}^{4}$ fragment is planar within $0.044(3) \AA$, and the $\mathrm{O}^{7}$ atom deviates from the above fragment by $-0.851(2) \AA]$. The $\mathrm{O}^{1}, \mathrm{O}^{2}, \mathrm{O}^{3}, \mathrm{C}^{3}, \mathrm{C}^{19}, \mathrm{C}^{25}$ and $\mathrm{C}^{26}$ atoms deviate from the abovementioned planar fragment by the values of $0.804(2), 1.364(2),-1.078(2), 1.322(3),-0.576(3)$, $1.366(4)$ and $-1.151(4) \AA$.

Considering that compounds $\mathbf{1 3}$ and 14 are formed simultaneously under very mild conditions $\left(-40^{\circ} \mathrm{C}\right)$ and the rearrangement of P -C-isomer 13 into $\mathrm{P}-\mathrm{O}$-isomer 14 is slow, it can
be assumed that they are formed from the common unstable phosphorane intermediate $\mathbf{A}$, which contains an oxaphosphirane cycle (Scheme 4). This intermediate is a product of the symmetry allowed [1+2]-cycloaddition reaction of phosphorus to the double bond of hexafluoroacetone. At low temperature, the cleavage of the three-membered ring occurs readily in two directions, $I$ and $I I$, which finally results in the formation of compounds 13 and 14 . The direction $I$, which includes $\mathrm{P}-\mathrm{O}$ bond cleavage and the formation of intermediate bipolar ions $\mathbf{B}$ and $\mathbf{C}$, is a kinetically controlled and reversible process. Direction II, which includes P-C bond cleavage and the formation of intermediate bipolar ions $\mathbf{D}$ and $\mathbf{E}$, irreversibly results in a thermodynamically controlled reaction product, the $\mathrm{P}-\mathrm{O}-$ isomer 14. Thus, the driving force of the PCO/POCrearrangements seems to be the greater thermodynamic stability of the resulting pentaalkoxyphosphorane $\mathbf{1 4}$ in comparison with its $\mathrm{P}-\mathrm{C}-\mathrm{analog}$ e 13. Furthermore, oxygen is more electronegative than carbon, and it is important for the stabilization of the phosphorus trigonal bipyramid, which increases its stability when acceptors are introduced to the phosphorus atom.

Due to the fact that racemic benzoin was used in the synthesis of phospholane 12 and in the reaction with hexafluoroacetone another chiral carbon $\left(\mathrm{C}^{4}\right)$ formation occurred, two $\mathrm{P}-\mathrm{C}$ diastereoisomers of isomer $\mathbf{1 3}$ should be formed. The formation of only one diastereoisomer indicates the high stereoselectivity of the second chiral center $\left(\mathrm{C}^{4}\right)$ formed, which is probably due to the rigid spatial requirements for the attack of the alkoxide-anion to the carbonyl group of the bipolar ion $\mathbf{B}$. The very important fact that the relative configuration of the chiral $\mathrm{C}^{3}$ and $\mathrm{C}^{4}$ atoms in the P-C- and P-O-isomers 13 and 14, according to XRD data, is the same indicates the highly stereoselective nature of the intramolecular PCO/POCrearrangement.

Hydrolysis of P-C-isomer 13 leads to the formation of dioxaphospholane 15, benzoin, and hexafluoroisopropanol. Benzoin and compound 15 were isolated by crystallization of the reaction mixture from diethyl ester. The structures of benzoin and hexafluoroisopropanol were proven by comparison of their spectral characteristics ( ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ and ${ }^{19} \mathrm{~F}$ NMR) with the literature. ${ }^{40-43}$ The structure of dioxaphospholane 15 was established based on the comparison of its spectral parameters with that described in the literature ${ }^{44,45}$ and XRD.

The geometry of the molecule in a crystal (solvate with one water molecule) is presented in Fig. 4. The five-membered cycle of molecule 15 has an envelope conformation, accordingly with a planar $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{8}$ fragment within $0.115(4) \AA$, and the $\mathrm{C}^{7}$ atom deviates from the abovementioned plane by $-0.492(8) \AA$. The $\mathrm{O}^{2}, \mathrm{C}^{9}$ and $\mathrm{C}^{12}$ atoms are located in axial positions (they deviate from the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{8}$ plane by $1.574(5),-1.990(8)$ and $1.552(8) \AA$, respectively). The $\mathrm{O}^{4}, \mathrm{C}^{10}$ and $\mathrm{C}^{11}$ atoms are located in equatorial positions and deviate from the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{8}$ plane by $-0.851(4), 0.20(1)$ and $-0.713(9) \AA$, respectively. Due to the presence of solvent water molecules in the crystal of $\mathbf{1 5}$, a classical hydrogen bond system is realized with the participation of the phosphoryl $\mathrm{O}^{4}$ oxygen and water molecule protons $\left[\mathrm{O}^{1 \mathrm{~S}}-\right.$ $\mathrm{H}^{1 \mathrm{~S}} \cdots \mathrm{O}^{4}$-interaction, the parameters are $\mathrm{O}^{1 \mathrm{~S}}-\mathrm{H}^{1 \mathrm{~S}} 0.72(9) \AA$,


Fig. 4 Geometry of molecule 15 in a crystal (solvate with water). Selected bond lengths ( $(\AA)$ and bond and torsion angles ( ${ }^{\circ}$ ): $\mathrm{P}^{1}-\mathrm{O}^{1}$ $1.568(6), P^{1}-O^{2} 1.533(7), P^{1}-O^{3} 1.572(6), P^{1}-O^{4} 1.477(6), O^{1}-P^{1}-O^{3}$ 98.6(2), $O^{1}-P^{1}-O^{2}$ 108.5(3), $O^{2}-P^{1}-O^{4}$ 113.5(3), $O^{1}-C^{7}-C^{8}-O^{3}$ 36.9(6), $C^{9}-C^{7}-C^{8}-C^{11} 33.6(8)$ and $C^{10}-C^{7}-C^{8}-C^{12} 34.5(8)$.
$\mathrm{H}^{1 \mathrm{~S}} \ldots \mathrm{O}^{4} 2.0(1) \AA, \mathrm{O}^{1 \mathrm{~S}} \cdots \mathrm{O}^{4} 2.75(1) \AA, \angle \mathrm{O}^{1 \mathrm{~S}}-\mathrm{H}^{1 \mathrm{~S}} \cdots \mathrm{O}^{4} 178(8)^{\circ}$, and symmetry operation $-1 / 2+x, 1 / 2-y, 1-z]$ and also between hydrogen at the $\mathrm{O}^{2}$ atom and water oxygen $\mathrm{O}^{1 \mathrm{~S}}\left[\mathrm{O}^{2}-\mathrm{H}^{2} \cdots \mathrm{O}^{1 \mathrm{~S}}\right.$. interaction, the parameters are $\mathrm{O}^{2}-\mathrm{H}^{2} 0.86(7) \AA, \mathrm{H}^{2} \cdots \mathrm{O}^{1 \mathrm{~S}} 1.61(7)$ $\AA, \mathrm{O}^{2} \cdots \mathrm{O}^{1 \mathrm{~S}} 2.46(1) \AA, \angle \mathrm{O}^{2}-\mathrm{H}^{2} \cdots \mathrm{O}^{1 \mathrm{~S}} 168(9)^{\circ}$, and symmetry operation $1+x, y, z]$. Using the classical hydrogen interactions, the molecules in the crystal 15 form ribbons along the $0 a$ crystallographic axis (see Fig. 5).

Mild stepwise hydrolysis of $\mathrm{P}-\mathrm{O}$-isomer 14 leads to the initial formation of dioxaphospholane 16. The ${ }^{31} \mathrm{P}$ NMR spectrum of this compound contains a doublet ( $\delta_{\mathrm{P}} 11.0 \mathrm{ppm},{ }^{3} J_{\mathrm{PCCH}} 5.9 \mathrm{~Hz}$ ) with a coupling constant from the proton at $\mathrm{C}^{3}$, which indicates the retention of the $\mathrm{P}-\mathrm{O}-\mathrm{C}^{3}$ fragment. Its ${ }^{13} \mathrm{C}$ NMR spectrum shows spin-spin coupling of all the methyl carbons with the phosphorus atom, which clearly points to the retention of the 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane cycle. This data are in accordance with the breaking of the $\mathrm{P}^{1}-\mathrm{O}^{2}$ and $\mathrm{P}^{1}-\mathrm{O}^{7}$ bonds in phosphorane $\mathbf{1 4}$ during hydrolysis. The result of the hydrolysis of phosphorane 14 differs by one for compound 11, which


Fig. 5 System of the intermolecular hydrogen bonds in a crystal of compound 15.
contains a 4,5-dimethyl-1,3,2-dioxaphospholane moiety. In the last case, the 2,3-butanediol elimination proceeds. ${ }^{37}$

The structure of phospholane 16 was confirmed using single crystal XRD. In Fig. 6, the geometry of the molecule in a crystal is presented (the main geometrical parameters, including bond length and valence and torsion angles of molecule $\mathbf{1 6}$ are presented in the ESI $\dagger$ ). The phosphorus atom has a distorted tetrahedral configuration. The dioxaphospholane cycle has an envelope conformation with a planar four-membered $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{7}$ fragment within $0.080(6) \AA$, and the $\mathrm{C}^{8}$ atom deviates from this plane by $0.510(9) \AA$ (see Fig. 7). The $\mathrm{O}^{2}, \mathrm{C}^{10}$ and $\mathrm{C}^{12}$ atoms are in axial positions (they deviate from the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{8}$ plane by the values of $1.260(5),-1.52(1)$ and $2.05(1) \AA$, respectively). The $\mathrm{O}^{4}$, $\mathrm{C}^{9}$ and $\mathrm{C}^{11}$ atoms are in equatorial positions (they deviate from the $\mathrm{O}^{1} \mathrm{P}^{1} \mathrm{O}^{3} \mathrm{C}^{8}$ plane by the values of $-1.265(6), 0.74(1)$ and $-0.05(1) \AA$, respectively). The presence of four methyl groups leads to a noticeable deviation of conformation along the $\mathrm{C}^{7}-\mathrm{C}^{8}$ bond from the regular staggered gauche conformation due to steric repulsion (the torsion angles $\mathrm{C}^{9} \mathrm{C}^{7} \mathrm{C}^{8} \mathrm{C}^{12}$ and $\mathrm{C}^{10} \mathrm{C}^{7} \mathrm{C}^{8} \mathrm{C}^{11}$ are equal to $-39(1)$ and $-36(1)^{\circ}$, respectively). The envelope conformation is probably realized in a solution for the investigated compound also, which is confirmed by the nonequivalence of these four methyl groups in NMR ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ spectra, and also by the different spin-spin coupling constants ${ }^{3} J_{\text {PCCC }}$, which depend on the P-C-C-C torsion angle values. The same situation is realized for the conformation along the $\mathrm{C}^{3}-\mathrm{C}^{4}$ bond (the torsion angles of $\mathrm{O}^{2} \mathrm{C}^{3} \mathrm{C}^{4} \mathrm{O}^{7}$ and $\mathrm{C}^{13} \mathrm{C}^{3} \mathrm{C}^{4} \mathrm{C}^{16}$ are $46.2(9)$ and $-45.2(9)^{\circ}$, respectively). The repulsion between the two phenyl groups probably has less meaning in comparison with the phenyl and hexafluoroisopropylhydroxy substituent repulsion, which leads to the same conformation along the $\mathrm{C}^{3}-$ $\mathrm{C}^{4}$ bond (the torsion angle of $\mathrm{C}^{5} \mathrm{C}^{4} \mathrm{C}^{3} \mathrm{C}^{13}$ is $-166.7(7)^{\circ}$ ). Due to the classical hydrogen bond, $\mathrm{O}^{6}-\mathrm{H}^{6} \cdots \mathrm{O}^{4}$, the molecules of $\mathbf{1 6}$ are connected in dimers, and thus, a 0D supramolecular structure is realized in the crystal [the parameters of the


Fig. 6 Geometry of molecule 16 in a crystal (racemate, $\mathrm{C}_{R}{ }^{3} \mathrm{C}_{S}{ }^{4}-$ enantiomer is shown). Selected bond lengths ( $\AA$ ) and bond and torsion angles ( ${ }^{\circ}$ ): $\mathrm{P}^{1}-\mathrm{O}^{1} 1.582(6), \mathrm{P}^{1}-\mathrm{O}^{2}$ 1.581(6), $\mathrm{P}^{1}-\mathrm{O}^{3} 1.583(7), \mathrm{P}^{1}-\mathrm{O}^{4}$ 1.460(6), $\mathrm{O}^{2}-\mathrm{C}^{3} 1.478(9), \mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{2}$ 101.2(3), $\mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{3} 99.6(3), \mathrm{O}^{1}-$ $\mathrm{P}^{1}-\mathrm{O}^{4}$ 118.9(4), $\mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{3}$ 109.6(3), $\mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{4}$ 112.7(3), $\mathrm{O}^{3}-\mathrm{P}^{1}-\mathrm{O}^{4}$ $113.4(4), P^{1}-O^{2}-C^{3}-C^{4} 163.2(5), O^{7}-C^{4}-C^{5}-O^{6} 165.2(6)$ and $O^{2}-C^{3}-$ $\mathrm{C}^{4}-\mathrm{O}^{7} 46.1(8)$.


Fig. 7 Conformation of 1,3,2-dioxaphospholane cycle along the $C^{7}-$ $C^{8}$ bond in 16 (acyclic substituent is omitted for clarity).
interaction are $\mathrm{O}^{6}-\mathrm{H}^{6} 0.66(6) \AA, \mathrm{H}^{6} \cdots \mathrm{O}^{4} 2.14(6) \AA, \mathrm{O}^{6} \cdots \mathrm{O}^{4}$ $2.76(1) \AA, \angle \mathrm{O}^{6}-\mathrm{H}^{6} \cdots \mathrm{O}^{4} 155(7)^{\circ}$, and symmetry operation $1-x$, $2-y,-z]$. The packing of the molecules in the crystal of 16 is also stabilized by the intramolecular bifurcate $\mathrm{O}^{7}-\mathrm{H}^{7} \cdots \mathrm{~F}^{1}$ and $\mathrm{O}^{7}-\mathrm{H}^{7} \cdots \mathrm{O}^{2}$ classical hydrogen bonds [the parameters are $\mathrm{O}^{7}-\mathrm{H}^{7}$ $0.87(8) \AA, H^{7} \cdots F^{1} 2.34(9) \AA, O^{7} \cdots F^{1} 2.860(9) \AA, \angle \mathrm{O}^{7}-\mathrm{H}^{7} \cdots \mathrm{~F}^{1}$ $119(8)^{\circ}$; and $\mathrm{H}^{7} \cdots \mathrm{O}^{2} 2.20(7) \AA, \mathrm{O}^{7} \cdots \mathrm{O}^{2} 2.722(8) \AA, \angle \mathrm{O}^{7}-\mathrm{H}^{7} \cdots \mathrm{O}^{2}$ $118(6)^{\circ}$ respectively, see Fig. 8].

Prolonged hydrolysis of phosphorane 14 leads to the cleavage of not only the exocyclic $\mathrm{P}^{1}-\mathrm{O}^{6}$ and $\mathrm{P}^{1}-\mathrm{O}^{7}$ bonds but also the $1,3,2$-dioxaphospholane P -O bonds. This process is accompanied by the formation of 2,3-dihydroxy-3-trifluoromethyl-4,4,4-trifluoro-1,2-diphenylbutylphosphate 17 and pinacol. It should be noted that phosphate $17\left(\delta_{\mathrm{P}}-1.4 \mathrm{ppm}\right.$, $\delta_{\mathrm{F}}-67.05$ and $\left.-67.82 \mathrm{ppm}\left(\mathrm{CDCl}_{3} / \mathrm{DMSO}-d_{6}, 3: 1\right)\right)$ exists in equilibrium with the cyclic form $19\left(\delta_{\mathrm{P}} 14.7 \mathrm{ppm}\left(\mathrm{CD}_{3} \mathrm{CN}\right), \delta_{\mathrm{F}}\right.$ -68.42 and $-69.98 \mathrm{ppm}\left(\mathrm{CDCl}_{3} / \mathrm{DMSO}-d_{6}, 3: 1\right)$ ) (Scheme 5) in a solution. ${ }^{37}$ The ratio of cyclic and acyclic phosphates in the reaction medium is close to $1: 10$; however, this equilibrium shifts to the formation of the cyclic derivative 19 upon heating $\left(40^{\circ} \mathrm{C}\right)$ and the ratio becomes $2: 1$. Long crystallization of the hydrolysis products from $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ allowed the isolation of the crystalline complex 18 of the acyclic monophosphate 17 with pinacol in a $2: 1$ ratio. The structure of complex 18 was


Fig. 8 The system of classical hydrogen bonds in the crystal of 16.
confirmed by XRD. The geometry of the complex in a crystal and atom numbering are shown in Fig. 9, and the main geometrical parameters (bond lengths and bond and torsion angles) are listed in the figure caption. The phosphorus atom has a distorted tetrahedral configuration, and the configuration of the chiral atoms is $\mathrm{C}_{S}{ }^{3} \mathrm{C}_{R}{ }^{4} / \mathrm{C}_{R}{ }^{3} \mathrm{C}_{S}{ }^{4}$. The conformations of the monophosphate 17 and pinacol molecules along the $\mathrm{C}^{4}-\mathrm{C}^{3}, \mathrm{C}^{5}-$ $\mathrm{C}^{4}$ and $\mathrm{C}^{6}-\mathrm{C}^{6 \mathrm{a}}$ bonds are shown in Fig. 10. All of them are closely related to the almost regular staggered species. The phenyl substituents are located in the gauche-conformation along the $\mathrm{C}^{4}-\mathrm{C}^{3}$ bond [the torsion angle of $\mathrm{C}^{13}-\mathrm{C}^{3}-\mathrm{C}^{4}-\mathrm{C}^{19}$ is $-50.1(6)^{\circ}$ ].


Fig. 9 Geometry of complex 18 in a crystal (solvate of molecule 17 with $1 / 2$ pinacol, racemate, and $C_{S}{ }^{3} C_{R}{ }^{4}$-enantiomer is shown). Selected bond lengths ( $\AA$ ) and bond and torsion angles ( ${ }^{\circ}$ ): $\mathrm{P}^{1}-\mathrm{O}^{1}$ 1.535(5), $\mathrm{P}^{1}-\mathrm{O}^{2} 1.588(4), \mathrm{P}^{1}-\mathrm{O}^{3} 1.551(4), \mathrm{P}^{1}-\mathrm{O}^{4} 1.489(4), \mathrm{O}^{1}-\mathrm{P}^{1}-\mathrm{O}^{2}$ 103.4(2), $O^{1}-P^{1}-O^{3}$ 102.6(3), $O^{1}-P^{1}-O^{4}$ 116.9(3), $O^{2}-P^{1}-O^{3}$ 109.1(2), $\mathrm{O}^{2}-\mathrm{P}^{1}-\mathrm{O}^{4} 111.3(2), \mathrm{O}^{2}-\mathrm{C}^{3}-\mathrm{C}^{4}-\mathrm{C}^{5} 58.8(6), \mathrm{P}^{1}-\mathrm{O}^{2}-\mathrm{C}^{3}-\mathrm{C}^{4}-168.4(3)$ and $C^{3}-C^{4}-C^{5}-C^{26}-163 \cdot 4(5)$.


Fig. 10 View of the conformations for the molecule (17) in front of the $C^{4}-C^{3}(a), C^{5}-C^{4}(b)$ and $C^{6}-C^{6 a}(c)$ bonds.

The trifluoromethyl groups have different orientations relative to the phenyl ring at the $\mathrm{C}^{4}$ atom (see Fig. 10) and therefore fluorine atoms exhibit non-equivalence in the ${ }^{19} \mathrm{~F}$ NMR spectrum owing to the anisotropy of the phenyl ring.

Due to the classical $\mathrm{O}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds of the molecules, 17 and pinacol form sheets along the $b 0 c$ crystallographic plane, and thus, a 2D supramolecular structure is realized in the crystal [the parameters of the interactions are $\mathrm{O}^{1}-\mathrm{H}^{1} \cdots \mathrm{O}(4)$ interaction: $\mathrm{O}^{1}-\mathrm{H}^{1} 0.86(6) \AA, \mathrm{H}^{1} \cdots \mathrm{O}^{4} 1.76(6) \AA, \mathrm{O}^{1} \cdots \mathrm{O}^{4} 2.547(6)$ $\AA, \angle \mathrm{O}^{1}-\mathrm{H}^{1}-\mathrm{O}^{4} 152(9)^{\circ}$, and symmetry operation $x, 3 / 2-y, 1 / 2+$ $z ; \mathrm{O}^{3}-\mathrm{H}^{3} \cdots \mathrm{O}^{5}$ interaction: $\mathrm{O}^{3}-\mathrm{H}^{3} 0.98(7) \AA, \mathrm{H}^{3} \cdots \mathrm{O}^{5} 1.68(7) \AA$, $\mathrm{O}^{3} \cdots \mathrm{O}^{5} 2.639(6) \AA, \angle \mathrm{O}^{3}-\mathrm{H}^{3}-\mathrm{O}^{5} 165(5)^{\circ}$, and symmetry operation $-1+x, 1+y,-1+z ; \mathrm{O}^{7}-\mathrm{H}^{7} \cdots \mathrm{O}^{4}$ interaction: $\mathrm{O}^{7}-\mathrm{H}^{7} 0.99(9)$ $\AA, \mathrm{H}^{7} \cdots \mathrm{O}^{4} 1.85(7) \AA, \mathrm{O}^{7} \cdots \mathrm{O}^{4} 2.802(6) \AA, \angle \mathrm{O}^{7}-\mathrm{H}^{7}-\mathrm{O}^{4} 159(8)^{\circ}$, and symmetry operation $x, 3 / 2-y, 1 / 2+z]$. The packing of the molecules 17 in the crystal of solvate 18 is also stabilized by the intramolecular $\mathrm{O}^{7}-\mathrm{H}^{7} \cdots \mathrm{~F}^{1}$ classical hydrogen bond [the parameters are $\mathrm{O}^{7}-\mathrm{H}^{7} 0.99(9) \AA, \mathrm{H}^{7} \cdots \mathrm{~F}^{1} 2.31(9) \AA, \mathrm{O}^{7} \cdots \mathrm{~F}^{1}$ 2.757(6) $\AA$, and $\angle \mathrm{O}^{7}-\mathrm{H}^{7}-\mathrm{F}^{1} 106(7)^{\circ}$, see ESI $\dagger$ ].

## Experimental

## 1-(2,3-Butylenedioxy)-6,6-bis(trifluoromethyl)-3,4-diphenyl-1,2,5,7-phosphatrioxabicyclo[2.2.1 ${ }^{1,4}$ heptane 13

Hexafluoroacetone ( $4.81 \mathrm{~g}, 30 \mathrm{mmol}$ ) was condensed into a $\mathrm{CCl}_{4} / \mathrm{CH}_{2} \mathrm{Cl}_{2}(1: 1)$ solution ( 40 mL ) of dioxaphosphole 12 $(10.4 \mathrm{~g}, 30 \mathrm{mmol})$ at $-40^{\circ} \mathrm{C}$. The reaction mixture was warmed up to $20^{\circ} \mathrm{C}(10 \mathrm{~h})$ and then evaporated under reduced pressure ( 14 Torr) to give a white precipitate of $\mathbf{1 3}$, which was filtered off and dried in vacuo ( 14 Torr). Yield $7.12 \mathrm{~g}(47 \%)$, mp 122-125 ${ }^{\circ} \mathrm{C}$. The filtrate was evaporated in vacuo ( 14 Torr ) under an argon atmosphere to give a pale yellow oil, which gradually crystallized under a pentane layer ( $-18{ }^{\circ} \mathrm{C}$ ). Clear white crystals of compound 13 were filtered off. Yield 3.62 g ( $24 \%$ ), mp 123-125 ${ }^{\circ} \mathrm{C}$. Anal. calcd for $\mathrm{C}_{23} \mathrm{H}_{23} \mathrm{~F}_{6} \mathrm{O}_{5} \mathrm{P}$ (524.12): C, $52.68 ; \mathrm{H}, 4.42$; P, 5.91. Found: C, 52.63 ; H, 4.39; P, 5.98. IR (KBr) $\left(\nu_{\max }, \mathrm{cm}^{-1}\right)$ : 2987, 2947, 1454, 1398, 1378, 1342, 1277, 1262, 1231, 1199, 1155, 1141, 1080, 1048, 1006, 979, 936, 883, 84, 816, 793, 770, $748,719,694,666,635,539,476 .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) /$ $\delta(\mathrm{ppm}): 7.30(\mathrm{~m}, 2 \mathrm{H}), 7.18(\mathrm{~m}, 5 \mathrm{H}), 7.10(\mathrm{~m}, 3 \mathrm{H}), 5.46(\mathrm{~d}, 1 \mathrm{H}$, ${ }^{3} J_{\mathrm{POCH}}=17.0 \mathrm{~Hz}, \mathrm{H}^{3}$ ), 1.49 (br. s, $12 \mathrm{H}, \mathrm{CH}_{3}$ ). ${ }^{13} \mathrm{C} /{ }^{13} \mathrm{C}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100.6 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), (hereinafter a view of signal in ${ }^{13} \mathrm{C}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum is in parentheses) $/ \delta_{\mathrm{C}}(\mathrm{ppm}): 135.74(\mathrm{~m}(\mathrm{~d})$, $\left.{ }^{3} J_{\mathrm{HCCC}}=7.7 \mathrm{~Hz},{ }^{2} J_{\mathrm{HCC}}=5.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{POCC}}=0.7 \mathrm{~Hz}, \mathrm{C}^{13}\right), 133.36(\mathrm{dt}$ (d), $\left.{ }^{3} J_{\mathrm{POCC}}=12.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=7.5 \mathrm{~Hz}, \mathrm{C}^{19}\right), 129.18\left(\mathrm{dt}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}}=\right.$ $\left.160.7 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=7.4 \mathrm{~Hz}, \mathrm{C}^{22}\right), 128.61\left(\mathrm{dm}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}}=161.0 \mathrm{~Hz}\right.$, ${ }^{3} J_{\mathrm{HCCC}}=7.2 \mathrm{~Hz}, \mathrm{C}^{16}$ ), 128.09 (br. dd (s), ${ }^{1} J_{\mathrm{HC}}=160.3 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}$ $\left.=7.4 \mathrm{~Hz}, \mathrm{C}^{15,17}\right), 127.90\left(\mathrm{dd}(\mathrm{s}),{ }^{1} \mathrm{~J}_{\mathrm{HC}}=161.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=7.0\right.$ $\mathrm{Hz}, \mathrm{C}^{21,23}$ ), 127.21 (br. ddd (s), ${ }^{1} \mathrm{JHC}_{\mathrm{HC}}=159.6 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HCCC}}=6.2-6.3$ $\left.\mathrm{Hz},{ }^{3} J_{\mathrm{HCCC}}=6.2-6.3 \mathrm{~Hz}, \mathrm{C}^{14,18}\right), 125.82\left(\mathrm{ddd}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}}=161.1 \mathrm{~Hz}\right.$, $\left.{ }^{3} J_{\mathrm{HCCC}}=7.4 \mathrm{~Hz},{ }^{3} \mathrm{H}_{\mathrm{HCCC}}=6.2 \mathrm{~Hz}, \mathrm{C}^{20,24}\right), 122.60\left(\mathrm{qd}(\mathrm{qd}),{ }^{1} J_{\mathrm{FC}}=\right.$ $285.8 \mathrm{~Hz},{ }^{2} J_{\mathrm{PCC}}=1.1 \mathrm{~Hz}, \mathrm{C}^{26}$ ), 121.71 (br. qd (qd), ${ }^{1} J_{\mathrm{FC}}=289.8$ $\left.\mathrm{Hz},{ }^{2} J_{\mathrm{PCC}}=5.7 \mathrm{~Hz}, \mathrm{C}^{25}\right), 99.76\left(\mathrm{ddm}(\mathrm{d}),{ }^{2} J_{\mathrm{POC}}=23.9 \mathrm{~Hz},{ }^{2} J_{\mathrm{HCC}}=\right.$ $\left.4.2-4.4 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=4.2-4.4 \mathrm{~Hz}, \mathrm{C}^{4}\right), 87.68\left(\mathrm{dmd}(\mathrm{d}),{ }^{1} J_{\mathrm{HC}}=\right.$ $\left.156.3 \mathrm{~Hz},{ }^{2} J_{\mathrm{POC}}=2.9 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=4.4 \mathrm{~Hz}, \mathrm{C}^{3}\right), 82.93\left(\mathrm{~m}(\mathrm{~d}),{ }^{2} J_{\mathrm{POC}}\right.$ $\left.=2.2 \mathrm{~Hz},{ }^{2} J_{\mathrm{HCC}}=4.2-4.4 \mathrm{~Hz}, \mathrm{C}_{\text {eq. }}{ }^{8}\right), 79.17\left(\mathrm{~m}(\mathrm{~d}),{ }^{2} J_{\mathrm{POC}}=2.9 \mathrm{~Hz}\right.$, ${ }^{2} J_{\mathrm{HCC}}=4.4 \mathrm{~Hz}, \mathrm{C}_{\mathrm{ax}}{ }^{7}$ ), 77.78 (d. sept (d. sept), ${ }^{1} J_{\mathrm{PC}}=154.8 \mathrm{~Hz}$,
${ }^{2} J_{\mathrm{FCC}}=30.7 \mathrm{~Hz}, \mathrm{C}^{6}$ ), 23.52 (br. qdq (br. d), ${ }^{1} J_{\mathrm{HC}}=127.3 \mathrm{~Hz}$, $\left.{ }^{3} J_{\mathrm{POCC}}=11.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=4.0 \mathrm{~Hz}, \mathrm{C}^{9-12}\right) .{ }^{19} \mathrm{~F}$ NMR $(376.5 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) / \delta_{\mathrm{F}}(\mathrm{ppm}):-68.44$ (q. d, ${ }^{4} J_{\mathrm{FCCCF}}=10.3 \mathrm{~Hz},{ }^{3} J_{\mathrm{PCCF}}=4.6$ $\mathrm{Hz}),-68.87\left(\mathrm{q},{ }^{4} J_{\mathrm{FCCCF}}=10.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{PCCF}}=2.3 \mathrm{~Hz}\right) .{ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\} /{ }^{31} \mathrm{P}$ NMR ( $\left.161.9 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) / \delta_{\mathrm{P}}(\mathrm{ppm}):-25.1\left(\mathrm{dd}(\mathrm{s}),{ }^{3} \mathrm{~J}_{\mathrm{PCCH}}=17.6\right.$ $\left.\mathrm{Hz},{ }^{3}{ }_{\mathrm{PCCF}}=1.9 \mathrm{~Hz}\right)$. ESI-MS $(\mathrm{m} / \mathrm{z}): 523.97$.

## 1-(2,3-Butylenedioxy)-5,5-bis(trifluoromethyl)-3,4-diphenyl-1,2,6,7-phosphatrioxabicyclo[2.2.1 $\left.{ }^{1,4}\right]$ heptane 14

A mixture of compound $13(6.00 \mathrm{~g}, 11.45 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20$ mL ) was kept for five days (control by ${ }^{31} \mathrm{P}$ NMR). After completion of the rearrangement, the reaction mixture was evaporated in vacuo ( 14 Torr) under an argon atmosphere to give a yellow oily residue, which was gradually crystallized during storage under a pentane layer $\left(-18{ }^{\circ} \mathrm{C}\right)$. The crystalline precipitate of $\mathbf{1 4}$ was filtered off and dried in vacuo ( 14 Torr). Yield 5.34 g ( $89 \%$ ), $\mathrm{mp} 125-127^{\circ} \mathrm{C}$. Anal. calcd for $\mathrm{C}_{23} \mathrm{H}_{23} \mathrm{~F}_{6} \mathrm{O}_{5} \mathrm{P}$ (524.12): C, 52.68 ; H, 4.42; P, 5.91. Found: C, 52.64; H, 4.40; P, 5.93. IR (KBr) ( $\nu_{\max }$, $\mathrm{cm}^{-1}$ ): 3067, 3036, 2984, 2938, 1500, 1460, 1452, 1396, 1378, 1288, 1241, 1164, 1103, 1042, 1014, 982, 949, 899, 879, 853, 833, 805, 783, 754, 738, 714, 713, 695, 666, 604, 581, 560, 498, 486, 461. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )/ $\delta(\mathrm{ppm}): 7.44(\mathrm{~m}, 1 \mathrm{H}), 7.30(\mathrm{~m}$, $1 \mathrm{H}), 7.17(\mathrm{~m}, 3 \mathrm{H}), 7.08(\mathrm{~m}, 5 \mathrm{H}), 5.72\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{POCH}}=19.2 \mathrm{~Hz}\right.$, $\left.\mathrm{H}^{3}\right), 1.52\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 1.51\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 1.43\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 1.38$ $\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) .{ }^{13} \mathrm{C} /{ }^{13} \mathrm{C}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(100.6 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) / \delta_{\mathrm{C}}(\mathrm{ppm}):$ $135.40\left(\mathrm{tt}(\mathrm{s}),{ }^{3} J_{\mathrm{HCCC}}=5.1-5.3 \mathrm{~Hz},{ }^{2} J_{\mathrm{HCC}}=2.2 \mathrm{~Hz}, \mathrm{C}^{13}\right), 131.08$ (dt (d), $\left.{ }^{3} J_{\mathrm{POCC}}=18.7 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=7.2 \mathrm{~Hz}, \mathrm{C}^{19}\right), 128.59(\mathrm{dm}(\mathrm{s})$, ${ }^{1} J_{\mathrm{HC}}=160.7 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=7.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HCCC}}=7.3 \mathrm{~Hz}, \mathrm{C}^{16}$ or $\mathrm{C}^{22}$ ), $128.56\left(\mathrm{dm}(\mathrm{s}),{ }^{1} \mathrm{~J}_{\mathrm{HC}}=160.7 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=7.3 \mathrm{~Hz},{ }^{3} \mathrm{JCCC}=7.3\right.$ $\mathrm{Hz}, \mathrm{C}^{16}$ or $\mathrm{C}^{22}$ ), $128.52\left(\mathrm{dm}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}}=161.4 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=7.3 \mathrm{~Hz}\right.$, ${ }^{3} J_{\mathrm{HCCC}}=7.3 \mathrm{~Hz}, \mathrm{C}^{14,18}$ ), 127.98 (br. dd (s), ${ }^{1} J_{\mathrm{HC}}=160.5 \mathrm{~Hz}$, ${ }^{3} J_{\mathrm{HCCC}}=7.2 \mathrm{~Hz}, \mathrm{C}^{23}$ ), 127.93 (br. dm (br. sept), ${ }^{1} J_{\mathrm{HC}}=160.5 \mathrm{~Hz}$, $\left.{ }^{5} J_{\mathrm{FCCCCC}}=1.9 \mathrm{~Hz}, \mathrm{C}^{24}\right), 127.76\left(\mathrm{dm}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}}=160.7 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=\right.$ $6.0-7.0 \mathrm{~Hz}, \mathrm{C}^{15,17}$ ), 127.13 (br. dd (s), ${ }^{1} J_{\mathrm{HC}}=161.4 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=$ $7.3 \mathrm{~Hz}, \mathrm{C}^{21}$ ), 126.90 br. dm (br. q), ${ }^{1} J_{\mathrm{HC}}=160.5 \mathrm{~Hz},{ }^{5} J_{\mathrm{FCCCCC}}=$ $\left.5.0 \mathrm{~Hz}, \mathrm{C}^{20}\right), 122.40\left(\mathrm{qd}(\mathrm{qd}),{ }^{1} J_{\mathrm{FC}}=286.4 \mathrm{~Hz},{ }^{3} J_{\mathrm{POCC}}=8.6 \mathrm{~Hz}\right.$, $\mathrm{CF}_{3}$ ), 121.08 (qd (qd), ${ }^{1} J_{\mathrm{FC}}=289.4 \mathrm{~Hz},{ }^{3} J_{\mathrm{POCC}}=2.7 \mathrm{~Hz}, \mathrm{CF}_{3}$ ), 83.41 (sept (sept), ${ }^{2} J_{\mathrm{CCF}}=29.3 \mathrm{~Hz}, \mathrm{C}^{5}$ ), $82.93\left(\mathrm{~m}(\mathrm{~d}),{ }^{2} J_{\mathrm{POC}}=2.2\right.$ $\left.\mathrm{Hz},{ }^{2} J_{\mathrm{HCC}}=3.6 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=3.8 \mathrm{~Hz}, \mathrm{C}_{\mathrm{eq}}{ }^{7}\right), 82.47\left(\mathrm{dm}(\mathrm{dq}),{ }^{1} J_{\mathrm{HC}}\right.$ $\left.=154.8 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{POC}}=2.9 \mathrm{~Hz},{ }^{4} J_{\mathrm{FCCCC}}=2.6-2.8 \mathrm{~Hz}, \mathrm{C}^{3}\right), 79.74(\mathrm{dt}$ (d), $\left.{ }^{2} J_{\mathrm{POC}}=20.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=3.7 \mathrm{~Hz}, \mathrm{C}^{4}\right), 79.30\left(\mathrm{~m}(\mathrm{~d}),{ }^{2} J_{\mathrm{POC}}=\right.$ $2.9 \mathrm{~Hz},{ }^{2} J_{\mathrm{HCC}}=3.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HCCC}}=3.6-3.7 \mathrm{~Hz}, \mathrm{Cax}^{8}{ }^{8}$ ), $23.72(\mathrm{qdq}(\mathrm{d})$, $\left.{ }^{1} J_{\mathrm{HC}}=127.6 \mathrm{~Hz},{ }^{3} J_{\mathrm{POCC}}=6.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=4.4 \mathrm{~Hz}, \mathrm{C}^{9}-\mathrm{C}_{\mathrm{eq}}{ }^{7}\right)$, 23.69 (qdq (d), ${ }^{1} J_{\mathrm{HC}}=127.6 \mathrm{~Hz},{ }^{3} J_{\mathrm{POCC}}=5.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HCCC}}=4.4 \mathrm{~Hz}$, $\mathrm{C}^{10}-\mathrm{C}_{\text {eq. }}{ }^{7}$ ), 23.54 (qdq (d), ${ }^{1} J_{\mathrm{HC}}=127.5 \mathrm{~Hz},{ }^{3} J_{\mathrm{POCC}}=7.7 \mathrm{~Hz}$, $\left.{ }^{3} J_{\mathrm{HCCC}}=4.4 \mathrm{~Hz}, \mathrm{C}^{11}-\mathrm{C}_{\mathrm{ax}}{ }^{8}\right), 23.36\left(\mathrm{qdq}(\mathrm{d}),{ }^{1} J_{\mathrm{HC}}=127.5 \mathrm{~Hz}\right.$, $\left.{ }^{3} J_{\mathrm{POCC}}=8.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=4.4 \mathrm{~Hz}, \mathrm{C}^{12}-\mathrm{C}_{\mathrm{ax}}{ }^{8}\right) .{ }^{19} \mathrm{~F}$ NMR (376.5 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) / \delta_{\mathrm{F}}(\mathrm{ppm}):-68.22\left(\mathrm{q},{ }^{4} J_{\mathrm{FCCCF}}=9.5 \mathrm{~Hz}\right),-72.35(\mathrm{q}$, ${ }^{4} J_{\text {FCCCF }}=9.5 \mathrm{~Hz}$ ). ${ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\} /{ }^{\beta 1} \mathrm{P}$ NMR ( $\left.161.9 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) / \delta_{\mathrm{P}}$ (ppm): -27.3 (d (s), $\left.{ }^{3}{ }_{\mathrm{POCH}}=20.4 \mathrm{~Hz}\right)$. ESI-MS $(\mathrm{m} / \mathrm{z}): 523.97$.

## Hydrolysis of compound 13

To a suspension of compound $13(1 \mathrm{~g}, 1.91 \mathrm{mmol})$ in diethyl ester ( 5 mL ), a solution of $0.1 \mathrm{~mL}(5.72 \mathrm{mmol})$ of water in 3 mL of diethyl ester was added dropwise with constant stirring. The resulting white crystalline precipitate of compound 15 (hydrate
with one $\mathrm{H}_{2} \mathrm{O}$ molecule) was filtered off and dried in vacuo (14 Torr). Yield 0.31 g ( $83 \%$ ), mp 190-192 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , DMF- $d_{7}$ ), $\delta: 8.72$ (br. s, $1 \mathrm{H}, \mathrm{OH}$ ), 1.41 (br. s, $12 \mathrm{H}, \mathrm{H}^{9-12}$ ). ${ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.9 \mathrm{MHz}, \mathrm{DMF}-d_{7}$ ), $\delta_{\mathrm{P}}: 10.6 \mathrm{ppm}(\mathrm{s})$. The ${ }^{1} \mathrm{H}$ NMR spectral data of an aliquot of the filtrate contain the benzoin and hexafluoroisopropanol signals. The structure of hexafluoroisopropanol was proven by a comparison of its spectral characteristics ( ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C},{ }^{19} \mathrm{~F}$ NMR) with previously published data. ${ }^{43}$ The filtrate was evaporated in vacuo (14 Torr) to give a white precipitate of benzoin, mp 132-134 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 600.0 MHz , acetone $\left.-d_{6} / \mathrm{CDCl}_{3}=2: 1\right) / \delta(\mathrm{ppm}): 8.03\left(\mathrm{~m}, 2 \mathrm{H}, X X^{\prime}\right.$-part of $A A^{\prime} X X^{\prime}$-subsystem, $\left.{ }^{3} J_{A X}={ }^{3} J_{A^{\prime} X^{\prime}}=7.5 \mathrm{~Hz}, \mathrm{H}^{20,24}\right), 7.56\left(\mathrm{tt}, 1 \mathrm{H},{ }^{3} J_{A M}\right.$ $={ }^{3} J_{A^{\prime} M}=7.5 \mathrm{~Hz},{ }^{4} J_{X M}={ }^{4} J_{X^{\prime} M^{\prime}}=1.5 \mathrm{~Hz}, M$-part of $A A^{\prime} M X X X^{\prime}-$ system, $\mathrm{H}^{22}$ ), 7.45 (br. dd, $2 \mathrm{H}, A A^{\prime}$-part of $A A^{\prime} X X^{\prime}$-subsystem, ${ }^{3} J_{A X}$ $\left.={ }^{3} J_{A^{\prime} X^{\prime}}=7.5 \mathrm{~Hz},{ }^{3} J_{A M}={ }^{3} J_{A^{\prime} M^{\prime}}=7.5 \mathrm{~Hz}, \mathrm{H}^{21,23}\right), 7.44\left(\mathrm{~m}, 2 \mathrm{H}, X X^{\prime}-\right.$ part of $A M M^{\prime} X X^{\prime}$-system, ${ }^{3} J_{X M}={ }^{3} J_{X^{\prime} M^{\prime}}=7.5 \mathrm{~Hz}, \mathrm{H}^{14,18}$ ), $7.32(\mathrm{br}$ dd, $2 \mathrm{H}, M M^{\prime}$-part of $A M M^{\prime} X X^{\prime}$-system, ${ }^{3} J_{X M}={ }^{3} J_{X^{\prime} M^{\prime}}=7.5 \mathrm{~Hz},{ }^{3} J_{A M}$ $={ }^{3} J_{A M^{\prime}}=7.5 \mathrm{~Hz}, \mathrm{H}^{15,17}$ ), $7.25\left(\mathrm{tt}, 1 \mathrm{H}, A\right.$-part of $A M M^{\prime} X X^{\prime}$-system, $\left.{ }^{3} J_{A M}={ }^{3} J_{A M^{\prime}}=7.5 \mathrm{~Hz},{ }^{4} J_{A X}={ }^{4} J_{A X^{\prime}}=1.5 \mathrm{~Hz}, \mathrm{H}^{16}\right), 6.13\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}^{3}\right)$, 4.93 (br. s, 1H, OH). ${ }^{13} \mathrm{C} /{ }^{13} \mathrm{C}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(150.0 \mathrm{MHz}\right.$, acetone- $d_{6} /$ $\left.\mathrm{CDCl}_{3}=2: 1\right) / \delta_{\mathrm{C}}(\mathrm{ppm}): 200.01$ (br. dt (s), ${ }^{2} \mathrm{JHC}^{3} \mathrm{C}^{4}=3.5 \mathrm{~Hz}$, $\left.{ }^{3} J_{\mathrm{HC}^{20,24} \mathrm{CC}^{4}}=3.3 \mathrm{~Hz}, \mathrm{C}^{4}\right), 140.75\left(\mathrm{tdd}(\mathrm{s}),{ }^{3} J_{\mathrm{HC}^{15,17} \mathrm{CC}^{13}}=7.5 \mathrm{~Hz}\right.$, $\left.{ }^{2} J_{\mathrm{HC}^{3} \mathrm{C}^{13}}=5.5 \mathrm{~Hz},{ }^{3} \mathrm{H}_{\mathrm{HOCC}^{13}}=1.3 \mathrm{~Hz}, \mathrm{C}^{13}\right), 135.36$ (br. $\mathrm{t}(\mathrm{s})$, $\left.{ }^{3} J_{\mathrm{HC}^{21,23} \mathrm{CC}^{19}}=7.4 \mathrm{~Hz}, \mathrm{C}^{19}\right), 134.27\left(\mathrm{dt}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}^{22}}=162.9 \mathrm{~Hz}\right.$, $\left.{ }^{3} J_{\mathrm{HC}^{20,24} \mathrm{CC}^{22}}=7.7 \mathrm{~Hz}, \mathrm{C}^{22}\right), 129.86$ (ddddd (s), ${ }^{1} J_{\mathrm{HC}^{20,24}}=161.3 \mathrm{~Hz}$, ${ }^{3} J_{\mathrm{HC}^{24,20} \mathrm{CC}^{20,24}}=7.6 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{22} \mathrm{CC}^{20,24}}=7.6 \mathrm{~Hz},{ }^{2} J_{\mathrm{HC}^{21,23}}{ }^{20,24}=1.7 \mathrm{~Hz}$, $\left.{ }^{4} J_{\mathrm{HC}^{4} \mathrm{CCC}^{20,24}}=1.3 \mathrm{~Hz}, \mathrm{C}^{20,24}\right), 129.52\left(\mathrm{br} . \mathrm{dm}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}^{15,17}}=161.5-\right.$ $\left.161.8 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{15,17} \mathrm{CC}^{17,15}}=6.0-7.0 \mathrm{~Hz}, \mathrm{C}^{15,17}\right), 129.41(\mathrm{dd}(\mathrm{s})$, $\left.{ }^{1} J_{\mathrm{HC}^{21,23}}=161.7 \mathrm{~Hz},{ }^{3} \mathrm{HCC}^{23,21} \mathrm{CC}^{21,23}=7.6 \mathrm{~Hz}, \mathrm{C}^{21,23}\right), 128.84(\mathrm{dtd}(\mathrm{s})$, $\left.{ }^{1} J_{\mathrm{HC}^{16}}=161.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{14,18} \mathrm{CC}^{16}}=7.6 \mathrm{~Hz},{ }^{5} J_{\mathrm{HC}^{3} \mathrm{CCCC}^{16}}=1.1 \mathrm{~Hz}, \mathrm{C}^{16}\right)$, $128.44\left(\mathrm{dm}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}^{14,18}}=162.4 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{18,14} \mathrm{CC}^{14,18}}=6.5-7.5 \mathrm{~Hz}\right.$, $\left.{ }^{3} J_{\mathrm{HC}^{16} \mathrm{CC}^{14,18}}=6.5-7.5 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{3} \mathrm{CC}^{14,18}}=4.5 \mathrm{~Hz}, \mathrm{C}^{14,18}\right)$, $76.94(\mathrm{dt}(\mathrm{s})$, $\left.{ }^{1} J_{\mathrm{HC}^{3}}=146.8 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{14,18}} \mathrm{CC}^{3}=4.0 \mathrm{~Hz}, \mathrm{C}^{3}\right) .{ }^{13} \mathrm{C}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR $(100.6$ $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ), $\delta_{\mathrm{C}}: 199.15$ (br. dt (s), ${ }^{2} J_{\mathrm{HC}^{3} \mathrm{C}^{4}}=3.3 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{20,24} \mathrm{CC}^{4}}=$ $\left.3.3 \mathrm{~Hz}, \mathrm{C}^{4}\right), 139.20\left(\operatorname{tdd}(\mathrm{~s}),{ }^{3} \mathrm{HC}^{15,17} \mathrm{CC}^{13}=7.3 \mathrm{~Hz},{ }^{2} J_{\mathrm{HC}^{3} \mathrm{C}^{13}}=5.5 \mathrm{~Hz}\right.$, ${ }^{3} J_{\mathrm{HOCC}^{13}}=2.2 \mathrm{~Hz}, \mathrm{C}^{13}$ ), 133.74 (br. $\mathrm{t}(\mathrm{s}),{ }^{3} J_{\mathrm{HC}^{21,2} \mathrm{CC}^{19}}=7.7 \mathrm{~Hz}, \mathrm{C}^{19}$ ), 134.07 (br. td (s), ${ }^{1} J_{\mathrm{HC}^{22}}=162.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HC}^{20,24} \mathrm{CC}^{22}}=7.7 \mathrm{~Hz}, \mathrm{C}^{22}$ ), 129.33 (ddddd (s), ${ }^{1} J_{\mathrm{HC}^{20,24}}=160.7 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{2,20} \mathrm{CC}^{20,24}}=7.6 \mathrm{~Hz}$, ${ }^{3} J_{\mathrm{HC}^{22} \mathrm{CC}^{20,24}}=7.6 \mathrm{~Hz},{ }^{2} J_{\mathrm{HC}^{21,23}} \mathrm{C}^{20,24}=1.4 \mathrm{~Hz},{ }^{4} J_{\mathrm{HC}^{4} \mathrm{CCC}^{20,24}}=1.2 \mathrm{~Hz}$, $\left.\mathrm{C}^{20,24}\right), 129.30$ (br. dd (s), ${ }^{1} J_{\mathrm{HC}^{15,17}}=161.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{15,17} \mathrm{CC}^{17,15}}=6.5-$ $7.0 \mathrm{~Hz}, \mathrm{C}^{15,17}$ ), 128.86 (dd (s), ${ }^{1} J_{\mathrm{HC}^{21,23}}=162.5 \mathrm{~Hz},{ }^{3} \mathrm{HC}^{23,21} \mathrm{CC}^{21,23}=$ $7.7 \mathrm{~Hz}, \mathrm{C}^{21,23}$ ), $128.76\left(\mathrm{dtt}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}^{16}}=161.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{14,18} \mathrm{CC}^{16}}=7.2\right.$ $\left.\mathrm{Hz},{ }^{2} J_{\mathrm{HC}^{15,17} \mathrm{C}^{16}}=1.5 \mathrm{~Hz}, \mathrm{C}^{16}\right), 127.96\left(\mathrm{dm}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}^{14,18}}=162.4 \mathrm{~Hz}\right.$, ${ }^{3} J_{\mathrm{HC}^{18,14} \mathrm{CC}^{14,18}}=6.5-7.5 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{16} \mathrm{CC}^{14,18}}=6.5-7.5 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{3} \mathrm{CC}^{14,18}}=$ $4.5 \mathrm{~Hz}, \mathrm{C}^{14,18}$ ), 76.42 (dtd (s), ${ }^{1} \mathrm{JHC}^{3}=146.8 \mathrm{~Hz},{ }^{3} J_{\mathrm{HC}^{14,18}} \mathrm{CC}^{3}=3.4$ $\left.\mathrm{Hz},{ }^{2} J_{\mathrm{HOC}^{3}}=1.5 \mathrm{~Hz}, \mathrm{C}^{3}\right)$.

## Hydrolysis of compound 14

To a suspension of compound $14(3.54 \mathrm{~g}, 6.75 \mathrm{mmol})$ in 10 mL of diethyl ester, a solution of $0.12 \mathrm{~mL}(6.75 \mathrm{mmol})$ of water in 5 mL of diethyl ester was added dropwise with constant stirring. The resulting white crystalline precipitate of compound 16 was filtered off and dried in vacuo (14 Torr). Yield 3.01 g ( $82 \%$ ), mp $155-156{ }^{\circ} \mathrm{C}$. Anal. calcd for $\mathrm{C}_{23} \mathrm{H}_{25} \mathrm{~F}_{6} \mathrm{O}_{6} \mathrm{P}$ (542.41): C, 50.93 ; H , 4.65; P, 5.71. Found: C, 50.94; H, 4.60; P, 5.73. IR (nujol) ( $\nu_{\max }$, $\mathrm{cm}^{-1}$ ): 3606, 3214, 2993, 1498, 1451, 1397, 1385, 1262, 1225,

1206, 1145, 1134, 1006, 993, 962, 930, 910, 815, 806, 724, 713, 700, 616, 594, 549, 497, 414. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, ~ D M F-d_{7}$ )/ $\delta(\mathrm{ppm}): 8.74$ (br. s, 1H, OH), $7.60\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HCCH}} 5.6 \mathrm{~Hz}, \mathrm{H}^{20,24}\right.$ ), $7.23\left(\mathrm{~m}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HCCH}}=6.7-7.7 \mathrm{~Hz},{ }^{5} \mathrm{JCCCCH}=1.5 \mathrm{~Hz}, \mathrm{H}^{14,18}\right), 7.11$ $\left(\mathrm{m}, 3 \mathrm{H}, \mathrm{H}^{21-23}\right), 7.05\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{H}^{15-17}\right), 6.25\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{POCH}}=7.6\right.$ $\mathrm{Hz}, \mathrm{H}^{3}$ ), 5.98 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{OH}$ ), 1.49 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Me}$ ), 1.42 ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{Me}$ ), 1.26 (s, 3H, Me). ${ }^{13} \mathrm{C} /{ }^{13} \mathrm{C}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100.6 \mathrm{MHz}, \mathrm{DMF}-d_{7}$ ) $/ \delta_{\mathrm{C}}(\mathrm{ppm})$ : 139.45 (br. td (br. s), ${ }^{3} J_{\mathrm{HCCC}}=6.2,{ }^{2} J_{\mathrm{HCC}}=5.2, \mathrm{C}^{13}$ ), 138.09 (ddd $(\mathrm{s}),{ }^{3} J_{\mathrm{HCCC}}=7.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=6.7 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=3.7 \mathrm{~Hz}, \mathrm{C}^{19}$ ), 130.91 (dddd (s), ${ }^{1} \mathrm{~J}_{\mathrm{HC}}=163.3 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=5.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HCCC}}=5.2$ $\left.\mathrm{Hz},{ }^{3} \mathrm{~J}_{\mathrm{HCCC}}=5.2 \mathrm{~Hz}, \mathrm{C}^{14,18}\right), \sim 129.2\left(\mathrm{v} . \mathrm{br} . \mathrm{d}(\mathrm{v} . \mathrm{br} . \mathrm{s}) \mathrm{C}^{20}\right), 128.53$ (dt (s), ${ }^{1} J_{\mathrm{HC}}=160.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=7.4 \mathrm{~Hz}, \mathrm{C}^{16}$ ), $128.13\left(\mathrm{dt}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}}\right.$ $\left.=160.0 \mathrm{~Hz},{ }^{3} \mathrm{JHCC}=7.7 \mathrm{~Hz}, \mathrm{C}^{22}\right), 127.69\left(\right.$ br. dd (s), ${ }^{1} \mathrm{~J}_{\mathrm{HC}}=161.8$ $\mathrm{Hz},{ }^{3} J_{\mathrm{HCCC}}=5.0-6.0 \mathrm{~Hz}, \mathrm{C}^{15,17}$ ), 127.37 (v. br. d (v. br. s), ${ }^{1} J_{\mathrm{HC}}$ $\left.\sim 160.0-162.0 \mathrm{~Hz}, \mathrm{C}^{21,23,24}\right), 124.80\left(\mathrm{q}(\mathrm{q}),{ }^{1} J_{\mathrm{FC}}=291.6 \mathrm{~Hz}, \mathrm{CF}_{3}\right.$ ), $124.58\left(\mathrm{q}(\mathrm{q}),{ }^{1} \mathrm{~J}_{\mathrm{FC}}=291.1 \mathrm{~Hz}, \mathrm{CF}_{3}\right), 89.33\left(\mathrm{~m}(\mathrm{~d}),{ }^{2} J_{\mathrm{POC}}=1.2 \mathrm{~Hz}\right.$, $\mathrm{C}^{7}$ or $\mathrm{C}^{8}$ ), $89.23\left(\mathrm{~m}(\mathrm{~s}), \mathrm{C}^{8}\right.$ or $\mathrm{C}^{7}$ ), 83.34 (sept (sept), ${ }^{2} \mathrm{~J}_{\mathrm{FCC}}=25.6$ $\mathrm{Hz}, \mathrm{C}^{5}$ ), 82.89 (br. dm (br. d), ${ }^{1} J_{\mathrm{HC}}=149.5 \mathrm{~Hz},{ }^{2} J_{\mathrm{POC}}=5.1 \mathrm{~Hz}$, $\mathrm{C}^{3}$ ), 81.75 (br. d (d), ${ }^{3} \mathrm{~J}_{\mathrm{POCC}}=10.0 \mathrm{~Hz}, \mathrm{C}^{4}$ ), 24.76, 24.27, 24.14 and 23.97 ppm (four qdq (four d), ${ }^{1} J_{\mathrm{HC}}=127.5,127.5,127.8$ and $127.9 \mathrm{~Hz},{ }^{3} J_{\mathrm{POCC}}=4.4,7.0,3.9$ and $6.5 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=4.3-4.4 \mathrm{~Hz}$, $\mathrm{C}^{9-12}$ ). ${ }^{19} \mathrm{~F}$ NMR (376.4 MHz, DMF- $d_{7}$ ) $/ \delta_{\mathrm{F}}(\mathrm{ppm}):-67.43$ ( q , $\left.{ }^{4} J_{\text {FCCCF }}=11.3 \mathrm{~Hz}\right),-68.19\left(\mathrm{q},{ }^{4} \int_{\text {FCCCF }}=11.3 \mathrm{~Hz}\right) .{ }^{31} \mathrm{P} /{ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 161.9 MHz, DMF- $d_{7}$ ) $/ \delta_{\mathrm{P}}(\mathrm{ppm}): 11.0\left(\mathrm{~d}(\mathrm{~s}),{ }^{3} \mathrm{~J}_{\mathrm{PCCH}}=5.9\right.$ $\mathrm{Hz}) .{ }^{13} \mathrm{C} /{ }^{13} \mathrm{C}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 100.6 MHz , DMSO- $d_{6}$ ) $/ \delta_{\mathrm{C}}(\mathrm{ppm}): 139.45$ (br. td (br. s), $\mathrm{C}^{13}$ ), $137.0\left(\mathrm{~m}(\mathrm{~s}), \mathrm{C}^{19}\right), 129.63\left(\mathrm{dddd}(\mathrm{s}),{ }^{1} J_{\mathrm{HCCC}}=\right.$ $160.0 \mathrm{~Hz},{ }^{3} \mathrm{JHCCC}=6.0-7.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=6.0-7.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HCCC}}=4.4$ $\mathrm{Hz}, \mathrm{C}^{14,18}$ ), $\sim 129.2$ (v. br. d (v. br. s) $\mathrm{C}^{20}$ ), 127.65 (dt (s), ${ }^{1} \mathrm{~J}_{\mathrm{HC}}=$ $\left.160.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=7.3 \mathrm{~Hz}, \mathrm{C}^{16}\right), 127.28\left(\mathrm{dt}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}}=160.0 \mathrm{~Hz}\right.$, $\left.{ }^{3} J_{\mathrm{HCCC}}=7.7 \mathrm{~Hz}, \mathrm{C}^{22}\right), 126.81\left(\mathrm{dd}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}}=160.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=\right.$ $6.6 \mathrm{~Hz}, \mathrm{C}^{15,17}$ ), $\sim 126.9$ (v. br. d (v. br. s), ${ }^{1} J_{\mathrm{HC}} \sim 160.0-162.0 \mathrm{~Hz}$, $\left.\mathrm{C}^{21,23,24}\right), 124.68\left(\mathrm{q}(\mathrm{q}),{ }^{1} J_{\mathrm{FC}}=292.0 \mathrm{~Hz}, \mathrm{CF}_{3}\right), 123.45\left(\mathrm{q}(\mathrm{q}),{ }^{1} J_{\mathrm{FC}}\right.$ $\left.=290.5 \mathrm{~Hz}, \mathrm{CF}_{3}\right), 89.31\left(\mathrm{~m}(\mathrm{~s}), \mathrm{C}^{7}\right.$ or $\left.\mathrm{C}^{8}\right), 88.18\left(\mathrm{~m}(\mathrm{~s}), \mathrm{C}^{8}\right.$ or $\left.\mathrm{C}^{7}\right)$, 82.01 (sept (sept), ${ }^{2} J_{\mathrm{FCC}}=25.6 \mathrm{~Hz}, \mathrm{C}^{5}$ ), 81.29 (br. dm (br. d), ${ }^{1} J_{\mathrm{HC}}$ $\left.=149.0 \mathrm{~Hz},{ }^{2} J_{\mathrm{POC}}=4.8 \mathrm{~Hz}, \mathrm{C}^{3}\right), 80.59\left(\right.$ br. d (d), ${ }^{3} J_{\mathrm{POCC}}=9.9 \mathrm{~Hz}$, $\mathrm{C}^{4}$ ), 24.24, 23.72, 23.55 and 23.37 (four qdq (four d), ${ }^{1} J_{\mathrm{HC}}=$ $127.6,127.6,128.4$ and $129.1 \mathrm{~Hz},{ }^{3} J_{\mathrm{POCC}}=3.7,7.0,3.3$ and 6.2 $\left.\mathrm{Hz},{ }^{3} J_{\mathrm{HCCC}}=3.0-3.3 \mathrm{~Hz}, \mathrm{C}^{9-12}\right) .{ }^{19} \mathrm{~F}$ NMR ( 376.4 MHz , DMSO- $d_{6}$ )/ $\delta_{\mathrm{F}}(\mathrm{ppm}):-66.49$ (br. q, ${ }^{4} \mathrm{~J}_{\mathrm{FCCCF}}=10.9 \mathrm{~Hz}$ ), -68.10 (br. q, ${ }^{4} \mathrm{~J}_{\mathrm{FCCCF}}$ $=10.9 \mathrm{~Hz}) .{ }^{31} \mathrm{P} /{ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 161.9 MHz, DMSO- $\left.d_{6}\right) / \delta_{\mathrm{P}}(\mathrm{ppm})$ : $10.7\left(\mathrm{~d}(\mathrm{~s}),{ }^{3} \mathrm{~J}_{\mathrm{PCCH}}=7.8 \mathrm{~Hz}\right)$. MALDI-MS $(\mathrm{m} / \mathrm{z}): 565.03(\mathrm{M}+\mathrm{Na})$, 580.93 ( $\mathrm{M}+\mathrm{K}$ ).

## Hydrolysis of compound 16

Compound $16(1.50 \mathrm{~g}, 2.77 \mathrm{mmol})$ was refluxed in a solution ( 15 mL ) of dioxane and $\mathrm{H}_{2} \mathrm{O}(2: 1)$ for 20 hours (control by ${ }^{31} \mathrm{P}$ NMR). ${ }^{31} \mathrm{P} /{ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR (161.9 MHz, dioxane/ $\delta_{\mathrm{P}}(\mathrm{ppm}):-1.2(\mathrm{~d}$ $(\mathrm{s}),{ }^{3} J_{\mathrm{PCCH}}=5.6 \mathrm{~Hz}$ ), 14.0 (br. s (s)). ${ }^{19}$ F NMR ( 376.4 MHz , $\left.\mathrm{CDCl}_{3}\right) / \delta_{\mathrm{F}}(\mathrm{ppm}):-67.39\left(\mathrm{q},{ }^{4} J_{\mathrm{FCCCF}}=10.9 \mathrm{~Hz}\right),-68.65(\mathrm{q}$, $\left.{ }^{4} J_{\text {FCCCF }}=10.9 \mathrm{~Hz}\right),-68.65\left(\mathrm{q},{ }^{4} J_{\text {FCCCF }}=10.9 \mathrm{~Hz}\right),-69.98(\mathrm{q}$, ${ }^{4} J_{\text {FCCCF }}=9.5 \mathrm{~Hz}$ ). After completion of the hydrolysis, the reaction mixture was evaporated in vacuo ( 14 Torr ) to give a yellow oily residue, which was crystallized from $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$. The crystalline precipitate of $\mathbf{1 8}$ (adduct with pinacol) was filtered off and dried in vacuo ( 14 Torr). Yield 1.01 g ( $63 \%$ ), mp 99-103 ${ }^{\circ} \mathrm{C}$. Anal. calcd for $\mathrm{C}_{23} \mathrm{H}_{29} \mathrm{~F}_{6} \mathrm{O}_{8} \mathrm{P}$ (578.44): C, 47.76; H, 5.05; P, 5.35.

Found: C, 47.74; H, 5.00; P, 5.31. IR (nujol) $\left(\nu_{\max }, \mathrm{cm}^{-1}\right.$ ): 3524, 3499, 3282, 3068, 2349, 1736, 1681, 1601, 1497, 1452, 1377, 1277, 1213, 1154, 1111, 1074, 1022, 1001, 967, 935, 761, 727, 711, 699, 624, 612, 541, 523, 494, 463. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CD}_{3} \mathrm{CN}\right) / \delta(\mathrm{ppm}): 7.46$ (br. d, $2 \mathrm{H}, \mathrm{H}^{20,24}$ ), $7.21\left(\mathrm{~d},{ }^{3}{ }_{\mathrm{HCCH}}=7.1\right.$ $\left.\mathrm{Hz}, 2 \mathrm{H}, \mathrm{H}^{14,18}\right), 7.10\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{H}^{19,20,21}\right), 7.04\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{H}^{15,16,17}\right)$, $6.09\left(\mathrm{~d},{ }^{3} J_{\mathrm{POCH}}=4.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}^{3}\right), 1.16(\mathrm{~s}, 12 \mathrm{H}, \mathrm{Me}$, pinacol). ${ }^{13} \mathrm{C} /{ }^{13} \mathrm{C}-\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(100.6 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right) / \delta_{\mathrm{C}}(\mathrm{ppm}): 137.98$ (br. td $\left.(\mathrm{s}),{ }^{2} J_{\mathrm{HCC}}=5.5, \mathrm{C}^{19}\right), 137.07$ (br. td (br. s), ${ }^{3} J_{\mathrm{HCCC}} 7.3 \mathrm{~Hz}, \mathrm{C}^{13}$ ), 131.10 (br. d (s), ${ }^{1} J_{\mathrm{HCCC}}=156.6 \mathrm{~Hz}, \mathrm{C}^{14,18}$ ), $\sim 127.9$ (v. br. d (v. br. s) $\mathrm{C}^{20,24}$ ), 128.71 (br. dt (s), ${ }^{1} \mathrm{~J}_{\mathrm{HC}} 161.4 \mathrm{~Hz}, \mathrm{C}^{16}$ ), 128.64 (br. dt (s), ${ }^{1} J_{\mathrm{HC}} 161.7 \mathrm{~Hz}, \mathrm{C}^{22}$ ), $128.10\left(\right.$ br. dd (s), ${ }^{1} J_{\mathrm{HC}}=158.5 \mathrm{~Hz},{ }^{3} J_{\mathrm{HCCC}}=$ $7.3 \mathrm{~Hz}, \mathrm{C}^{15,17}$ ), 127.85 and 126.74 (two v. br. d (two v. br. s), $\mathrm{C}^{20,24}$ and $\left.\mathrm{C}^{21,23}\right), 124.35\left(\mathrm{q}(\mathrm{q}),{ }^{1} \mathrm{~J}_{\mathrm{FC}}=289.4 \mathrm{~Hz}, \mathrm{CF}_{3}\right), 124.18\left(\mathrm{q}(\mathrm{q}),{ }^{1} J_{\mathrm{FC}}\right.$ $=290.9 \mathrm{~Hz}, \mathrm{CF}_{3}$ ), $90.34\left(\mathrm{~m}(\mathrm{~s})\right.$, pinacol), 83.79 (sept (sept), ${ }^{2} J_{\mathrm{FCC}}$ $\left.=25.7 \mathrm{~Hz}, \mathrm{C}^{5}\right), 83.12\left(\mathrm{~d} . \mathrm{m}(\mathrm{d}),{ }^{1} J_{\mathrm{HC}}=151.5 \mathrm{~Hz},{ }^{2} J_{\mathrm{POC}}=2.6 \mathrm{~Hz}\right.$, $\left.\mathrm{C}^{3}\right), 81.87\left(\mathrm{~m}(\mathrm{~d}),{ }^{3} J_{\mathrm{POCC}}=8.1 \mathrm{~Hz}, \mathrm{C}^{4}\right), 25.16\left(\mathrm{q}(\mathrm{s}),{ }^{1} J_{\mathrm{HC}}=125.4\right.$, $\mathrm{CH}_{3}$, pinacol). ${ }^{19}$ F NMR ( $\left.376.4 \mathrm{MHz}, \mathrm{CDCl}_{3} / \mathrm{DMSO}_{6}(3: 1)\right) / \delta_{\mathrm{F}}$ (ppm): -67.05 (q, $\left.{ }^{4} J_{\text {FCCCF }}=11.2 \mathrm{~Hz}\right),-67.82\left(\mathrm{q},{ }^{4} \mathrm{~J}_{\mathrm{FCCCF}}=10.2\right.$ $\mathrm{Hz}) .{ }^{31} \mathrm{P} /{ }^{31} \mathrm{P}-\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.9 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right) / \delta_{\mathrm{P}}(\mathrm{ppm}):-1.4(\mathrm{br} . \mathrm{s}$ (s)).

## Crystal structure determination

Crystal structures were determined by X-ray diffraction of suitable monocrystals. Crystal data were collected at 296 K using graphite monochromatic $\operatorname{MoK}_{\alpha}(0.71073 \AA$ ) radiation and $\omega$ scan. Data collection images were indexed, integrated, and scaled using the APEX2 data reduction package. ${ }^{46}$ Multi-scan empirical absorption corrections were applied to all data sets, where appropriate, using the SADABS program. ${ }^{47}$ The structures were solved and refined using the SHELX ${ }^{48}$ program. All crystal structure pictures were created using Mercury CSD 2.4. ${ }^{49}$

## Crystal data for 13

$\mathrm{C}_{23} \mathrm{H}_{23} \mathrm{~F}_{6} \mathrm{O}_{5} \mathrm{P}, M=524.38$, monoclinic, $a=9.485(6), b=$ 11.002(7), $c=12.115(8) \AA, \beta=101.517(8)^{\circ}, V=1239(1) \AA^{3}, T=$ 296 K , space group $P 2_{1}$ (no. 4), $Z=2,12827$ reflections measured, 4529 unique ( $R^{\text {int }}=0.071$ ), which were used in all calculations. Final indices $R_{1}=0.0667, \mathrm{w} R_{2}=0.1629$ for 2921 reflections with $I>2 \sigma(I) ; R_{1}=0.1100, \mathrm{w} R_{2}=0.2021$ for all data.

## Crystal data for 14

$\mathrm{C}_{23} \mathrm{H}_{23} \mathrm{~F}_{6} \mathrm{O}_{5} \mathrm{P}, M=524.38$, orthorhombic, $a=12.650(5), b=$ 16.695(6), $c=22.988(9) \AA, V=4855(3) \AA^{3}, T=296 \mathrm{~K}$, space group $P b c a$ (no. 61), $Z=8,28292$ reflections measured, 4766 unique ( $R^{\text {int }}=0.066$ ), which were used in all calculations. Final indices $R_{1}=0.0520, \mathrm{w} R_{2}=0.1426$ for 2856 reflections with $I>$ $2 \sigma(I) ; R_{1}=0.0985, \mathrm{w} R_{2}=0.1825$ for all data.

## Crystal data for 15

$\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{O}_{5} \mathrm{P}, M=198.15$, orthorhombic, $a=6.39(2), b=10.62(3)$, $c=14.67(3) \AA, V=995(4) \AA^{3}, T=296 \mathrm{~K}$, space group $P 2_{1} 2_{1} 2_{1}$ (no. 19), $Z=4,5025$ reflections measured, 1949 unique $\left(R^{\mathrm{int}}=\right.$ 0.068 ), which were used in all calculations. Final indices $R_{1}=$
$0.0499, \mathrm{w} R_{2}=0.1437$ for 1316 reflections with $I>2 \sigma(I) ; R_{1}=$ $0.0907, \mathrm{w} R_{2}=0.1841$ for all data.

## Crystal data for 16

$\mathrm{C}_{23} \mathrm{H}_{25} \mathrm{~F}_{6} \mathrm{O}_{6} \mathrm{P}, M=542.40$, triclinic, $a=10.788(13), b=$ 10.889(13), $c=12.329(15) \AA, \alpha=70.63(2), \beta=71.74(2), \gamma=$ $67.88(2)^{\circ}, V=1236(3) \AA^{3}, T=296 \mathrm{~K}$, space group $P \overline{1}$ (no. 2), $Z=$ 2,4706 reflections measured, which were used in all calculations. Final indices $R_{1}=0.0880, \mathrm{w} R_{2}=0.2734$ for 2147 reflections with $I>2 \sigma(I) ; R_{1}=0.1946, \mathrm{w} R_{2}=0.3522$ for all data.

## Crystal data for 18

$\mathrm{C}_{17} \mathrm{H}_{15} \mathrm{~F}_{6} \mathrm{O}_{6} \mathrm{P} \quad 0.5 \mathrm{C}_{6} \mathrm{H}_{14} \mathrm{O}_{2}, \quad M=519.34$, monoclinic, $a=$ 18.721(8), $b=13.944(6), c=8.706(4) \AA, \beta=95.489(8)^{\circ}, V=$ $2262(2) \AA^{3}, T=296 \mathrm{~K}$, space group $P 2_{1} / c$ (no. 14), $Z=4,11470$ reflections measured, 4448 unique ( $R^{\mathrm{int}}=0.152$ ), which were used in all calculations. Final indices $R_{1}=0.0773, \mathrm{w} R_{2}=0.1632$ for 1683 reflections with $I>2 \sigma(I) ; R_{1}=0.2229, \mathrm{w} R_{2}=0.2372$ for all data.

## Conclusions

It was shown that the reaction of 4,4,5,5-tetramethyl-2-(2-oxo-1,2-diphenyl)ethoxy-1,3,2-dioxaphospholane 12 with hexafluoroacetone results in the simultaneous formation of regioisomeric cage ( $\mathrm{P}-\mathrm{C} / \mathrm{P}-\mathrm{O}$ )-phosphoranes 13 and 14 in the ratio of $10: 1$. In dichloromethane solution $\left(20{ }^{\circ} \mathrm{C}, 5\right.$ days), the rearrangement of $\mathrm{P}-\mathrm{C}$-isomer $\mathbf{1 3}$ to $\mathrm{P}-\mathrm{O}$-isomer $\mathbf{1 4}$ proceeds with high stereoselectivity ( $>96 \%$ ). The $\mathrm{P}-\mathrm{C}-\mathrm{isomer}$ hydrolysis unexpectedly leads to the formation of 2-hydroxy-4,4,5,5-tetramethyl-2-oxo-1,3,2-dioxaphospholane with high chemoselectivity. Hydrolysis of the $\mathrm{P}-\mathrm{O}$-isomer results in the formation of one stereoisomer of 2-(2,3-dihydroxy-1,2-diphenyl-3-trifluoromethyl-4,4,4-trifluorobutyloxy)-4,4,5,5-tetramethyl-2-oxo-1,3,2-dioxaphos pholane with the same configurations for the $\mathrm{C}^{3}$ and $\mathrm{C}^{4}$ atoms, and further hydrolysis of this compound yields 2,3-dihydroxy-3-trifluoromethyl-4,4,4-trifluoro-1,2-diphenyl butylphosphate 17 and pinacol.

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