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Introduction

Pentacoordinated phosphorus compounds are key intermediates in phosphoryl group transfer reactions, which are important in the processes of cell viability¹⁻⁷ 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 Mitsunobu¹⁷⁻¹⁹ 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(m)-derivatives to unsaturated systems, various reactions of tetracoordinated phosphorus and substitution reactions at P(v)^{28,29} should be noted.

Synthesis, crystal structure and hydrolysis of novel isomeric cage (P–C/P–O)-phosphoranes on the basis of 4,4,5,5-tetramethyl-2-(2-oxo-1,2diphenylethoxy)-1,3,2-dioxaphospholane and hexafluoroacetone[†]

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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 (P-C/P-O)-phosphoranes, the structures of which are unequivocally confirmed by XRD. The rearrangement of the P–C-isomer to P–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-1,3,2-dioxaphospholane 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-1,2-diphenylbutylphosphate 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.

Recently, we developed a new approach for the preparation of phosphoranes based on the cascade reactions of P(III)-derivatives, containing an unsaturated moiety with carbonyl compounds, which leads to P(v)–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 P^+ –C–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 2–4 bearing the P–C-bond.^{30–32}

Scheme 2 demonstrates the synthetic potential of the intramolecular cascade cyclization of P(m)-derivatives 1 under the



Scheme 1 Use of P(m)-derivatives bearing an exocyclic C=O or C=N bond in the synthesis of cage phosphoranes.

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Scheme 2 Reaction of P(III)-derivatives 1 bearing an exocyclic C=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 shown³⁷ that the inclusion of a phosphorus(m) 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-dioxaphospholane⁹ with hexafluoro acetone (Scheme 3). PCO-phosphorane **10** is subjected to intramolecular PCO/POC-rearrangement during storage (CH₂Cl₂, 20 °C, 30 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 (CCl_4 , -40 °C) with the simultaneous formation of two isomeric pentacoordinated phosphorus

species 13 and 14 (Scheme 4), which have two high-field signals at $\delta_{\rm P}$ –24.5 and $\delta_{\rm P}$ –26.5 ppm in a ratio of 10 : 1 in their ³¹P– {¹H} 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 13 during storage. It manifests itself as a doublet in the high-field region (CCl₄, $\delta_{\rm P}$ –25.1 ppm, ${}^{3}J_{\rm PCCH}$ = 15.6 Hz) of the ³¹P-{¹H} NMR spectrum. Taking into account the spectral data (see ESI[†]), 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 ¹⁹F NMR spectrum contains two signals at $\delta_{\rm F}$ –68.48 (qd, ${}^{4}J_{\rm FCCCF}$ = 10.3 Hz, ${}^{3}J_{\rm PCCF}$ = 4.6 Hz) and $\delta_{\rm F}$ –68.94 ppm (qd, ${}^{4}J_{\text{FCCCF}} = 10.3 \text{ Hz}$, ${}^{3}J_{\text{PCCF}} 2.3 \text{ Hz}$) with an equal integral intensity, which correspond to the non-equivalent fluorine atoms of CF₃-groups. In contrast to the abovementioned phosphite 9, which is a hexafluoroacetone system, the formation of PC-phosphorane 13 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 $P_R^{-1}C_R^{-3}C_S^{-4}$. A small deviation in the phosphorus atom from the $O^3O^2O^6$ plane [by -0.114(2) Å] allows us to conclude that the phosphorus atom has a slightly distorted trigonal bipyramidal configuration with a planar 0.085(2) Å base, formed by the P¹, O², O³ and C⁶ atoms. The O¹ and O⁷ atoms located in the apical positions deviate from this plane by -1.696 (5) and 1.619(5) Å, respectively [bond angle of \hat{f}^1 – P^1 – O^7 is equal to 172.4



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 (Å), and bond and torsion angles (°): $P^1-O^1 1.613(5)$, $P^1-O^2 1.619(5)$, $P^1-O^3 1.583(5)$, $P^1-O^7 1.711(5)$, $P^1-C^6 1.930(7)$, $O^1-P^1-O^2 96.3(3)$, $O^1-P^1-O^3 92.7(3)$, $O^1-P^1-O^7 172.4(3)$, $O^1-P^1-C^6 92.8(3)$, $O^2-P^1-O^3 120.9(3)$, $O^2-P^1-O^7 90.3(2)$, $O^2-P^1-C^6 100.7(3)$, $O^3-P^1-O^7 85.7(2)$, $O^3-P^1-C^6 136.9(3)$, $O^7-P^1-C^6 83.3(3)$, $C^9-C^7-C^8-C^{12}-161.4(8)$, $P^1-O^7-C^4-C^{19} 177.5(5)$, $C^{13}-C^3-C^4-C^{19} 46.2(8)$ 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.

(3°)]. One of the two trifluoromethyl groups ($C^{25}F_3$) is almost in this plane [C^{25} atom deviation from it is 0.21(1) Å]. The O¹–P¹–O³, O¹–P¹–O², O¹–P¹–C⁶, O²–P¹–O⁷, O⁷–P¹–C⁶ and O³–P¹–O⁷ bond angles vary within the limits of 83.3(3)–96.9(3)°. The O²–P¹–C⁶, O²–P¹–O³ and O³–P¹–C⁶ bond angle sum in the pyramid base is equal to 358.5(2)° and points to a trigonal bipyramidal phosphorus configuration close to an almost regular configuration. The P¹–O³ equatorial bond length is slightly smaller [1.583(5) Å] than the P¹–O¹ and P¹–O⁷ axial bond lengths of [1.613(3) and 1.711(5) Å].

The concurrence of the P^1 - O^1 and P^1 - O^7 axial bond length sum [3.324(5) Å] and $O^1 \cdots O^7$ distance [3.317(7) Å] can be considered as evidence of the regular trigonal bipyramidal phosphorus configuration. The P¹-C⁶ bond length is equal to 1.930(7) Å. A five-membered dioxaphospholane cycle occupies the axial-equatorial position in the trigonal bipyramid (O^1 is axial and O^3 is equatorial), its conformation is *envelope*, where four atoms, O¹, P¹, O³ and C⁸, lie in one plane [planar within 0.004(5) Å], and the C⁷ atom deviates from this plane by 0.518(9)Å. The C^9 and C^{12} atoms deviate from this plane by 2.05(1) and -1.43(1) Å, respectively, and they occupy axial positions in the cycle. The C¹⁰ and C¹¹ atoms also deviate from the O¹P¹O³C⁸ plane by -0.05(1) and 0.91(1) Å, respectively, and are located in equatorial positions. The O² and C⁶ atoms deviate in opposite sides from the $O^{1}P^{1}O^{3}C^{7}$ plane [their deviations are 1.377(5) and -1.297(8) Å, respectively] and occupy equatorial and axial positions in the five-membered cycle. The C¹⁰ and O⁷ deviations are minimal [they deviate by -0.05(1) and -0.213(5) Å, respectively] and we can assume that they lie in the O¹P¹O³C⁸ plane.

The O¹P¹O³C⁸ fragment can also be considered as a part of the most elongated seven-membered approximately planar $C^{8}O^{3}P^{1}O^{1}O^{7}C^{4}C^{19}$ system [planar within 0.135(5) Å]. The plane of the phenyl substituent in the fourth position of the bicycloheptane **13** is slightly turned in the dihedral angle of $6.2(5)^{\circ}$ relative to the seven-membered fragment. The conformation of the five-membered $P^1O^2C^3C^4O^7$ cycle of molecule 13 is *envelope* (Fig. 1). It includes a four-membered plane $P^1O^2C^3C^4$ fragment [planar within 0.025(5) Å], and the O^7 atom deviates from this plane by 0.760(5) Å. The O^1 , O^3 , O^5 , C^6 , C^{13} and 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)Å, respectively. This is due to fact that the C^{13} and 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 P¹C⁶O⁵C⁴O⁷ ring of the rigid bicycloheptane scaffold is a slightly distorted *envelope*. The four-membered P¹C⁶O⁵C⁴ fragment is planar within 0.066(5) Å, and the O^7 atom deviates from this plane by -0.853(5) Å. The O¹, O², O³, C³, C¹⁹, C²⁵ and C²⁶ 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)Å, respectively.

During storage in very polar dichloromethane at 20 °C for about five days, compound 13 underwent a gradual conversion to compound 14 (after four days, the ratio of compounds 13/14 was 1 to 20). Fig. 2 shows the spectral image of this process according to ³¹P–{¹H} NMR. The figure shows that phosphorane 13 (CH₂Cl₂, $\delta_{\rm P}$ –25.0 ppm) was completely converted to pentaoxyphosphorane 14 (CH₂Cl₂, $\delta_{\rm P}$ –26.7 ppm), 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-butylenedioxy)-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 ¹³C-{¹H} NMR spectrum of compound 14, the carbon atom bonded to CF₃-groups resonates at 83.41 ppm as a septet with coupling through two bonds from fluorine ${}^{2}J_{CCF} = 29.3$ Hz), unlike the spectrum of compound 13 in which the oxygenated carbon in the $OC(CF_3)_2$ fragment manifests itself as a doublet of septets at 77.78 ppm with direct spin-spin coupling from phosphorus (${}^{1}J_{PC} = 154.8 \text{ Hz}, {}^{2}J_{FCC} = 30.7 \text{ Hz}$). The signals of the CF₃-groups in the ¹⁹F NMR spectrum of compound 14 appear as two quartets at $\delta_{\rm F}$ –68.22 ppm and -72.35 ppm (⁴ $J_{\text{FCCCF}} = 9.5$ Hz).

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†). The configuration of the chiral atoms is $P_R^{\ 1}C_R^{\ 3}C_S^{\ 4}/P_S^{\ 1}$ - $C_S^{\ 3}C_R^{\ 4}$ (racemate). The meaningless deviation of the phosphorus atom from the O³O²C⁶ plane by -0.0580(7) Å allows to conclude that the geometry of phosphorus in molecule **14** is a slightly distorted trigonal bipyramid with a planar base [within 0.043(2) Å], where the P¹, O², O³, C⁶ atoms are located. The O¹ and O⁷ atoms located in apical positions deviate from



Fig. 2 Conversion of P–C-phosphorane 13 to P–O-species 14 according to 31 P– 1 H} NMR spectra (CH₂Cl₂, in one day, and after two, three and five days).

1 day

2 days

3 days

5 days

-40



Fig. 3 Geometry of molecule 14 in a crystal (racemate, $P_5^{-1}C_5^{-3}C_R^{-4}$ enantiomer is shown). The base of the trigonal bipyramid is shown by thin lines. Selected bond lengths (Å) and bond and torsion angles (°): $P^1-O^1 1.625(2), P^1-O^2 1.606(2), P^1-O^3 1.582(2), P^1-O^6 1.647(2), P^1-O^7 1.700(2), O^1-P^1-O^2 92.1(1), O^1-P^1-O^3 92.4(1), O^1-P^1-O^7 177.5(1), O^1-P^1-O^6 91.6(1), O^2-P^1-O^3 126.4(1), O^2-P^1-O^7 90.4(1), O^2-P^1-O^6 105.8(1), O^3-P^1-O^7 86.1(1), O^3-P^1-O^6 127.4(1), O^6-P^1-O^7 87.8(1), C^9-C^7-C^8-C^{11} -164.4(4), P^1-O^7-C^4-C^{19} 178.8(2), C^{13}-C^3-C^4-C^{19} -40.9(3) and O^7-C^4-C^{19}-C^{20} 10.0(4).$

the above plane by the values of -1.625(2) and 1.700(2) Å [the valence angle of $O^1 - P^1 - O^7$ is equal to $177.5(1)^\circ$]. The values of the valence angles O¹-P¹-O³, O¹-P¹-O², O¹-P¹-O⁶, O²-P¹-O⁷, O⁶-P¹-O⁷ and O³-P¹-O⁷ vary within the limits of 86.1(1)-92.4(1)°, and the sum of the valence angles of $O^2-P^1-O^6$, $O^2-P^1-O^6$ O^3 and $O^3-P^1-O^6$ 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 P¹-O², P¹-O³ and P¹-O⁶ bonds [1.606(2), 1.582(2), and 1.647(2) Å, respectively] are slightly shorter than the axial P^1-O^1 and P^1- O⁷ bonds [1.625(2) and 1.700(2) Å, respectively]. The fact of practical coincidence of the P¹-O¹ and P¹-O⁷ axial bond values sum [3.325(5) Å] and $O^1 \cdots O^7$ distance [3.323(7) Å] is in favor of the regular trigonal bipyramid configuration. The fivemembered tetramethyldioxaphospholane cycle occupies the axial-equatorial position in the trigonal bipyramid (O^1 atom is axial and O³ atom is equatorial). Its conformation is a distorted *envelope*, where four O^1 , P^1 , O^3 and C^7 atoms lie in one plane [planar within 0.0482(7) Å], and the C^8 atom deviates from the above plane by 0.422(4) Å. The C⁹ and C¹² atoms deviate from the plane to the opposite sides by the rather significant distances of -1.525(5) and 1.963(6) Å, respectively (they occupy axial positions in the cycle), and the C¹⁰ and C¹¹ atoms also deviate by the different values of 0.758(5) and -0.178(6) Å (they occupy equatorial positions in the cycle). The O^2 and O^6 atoms deviate to opposite sides from the $O^{1}P^{1}O^{3}C^{7}$ plane and occupy equatorial and axial positions in the five-membered cycle [their deviations are 1.182(2) and -1.406(2) Å, respectively]. The O⁷ atom deviation is minimal [-0.213(5) Å]; thus, it can be concluded that this atom lies in the O¹P¹O³C⁷ plane. Moreover, it should be noticed that the O¹P¹O³C⁷ fragment is turned to be part of the more extended planar moiety of а $C^{7}O^{3}P^{1}O^{1}O^{3}O^{7}C^{4}C^{19}$ in the molecule [planar within 0.054(4) Å]. The plane of the phenyl substituent position $4(C^{19-24})$ 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 $9.2(2)^{\circ}$]. The conformation of the five-membered $P^1O^2C^3C^4O^7$ cycle of the rigid bicycloheptane system of molecule 14 is an envelope [it contains a planar fourmembered $P^1O^2C^3C^4$ fragment within 0.033(2) Å, and the O⁷ atom deviates from it by 0.806(2) Å]. The \hat{I}^1 , O^3 , C^5 , O^6 , C^{13} and C¹⁹ 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) Å, respectively. The fact that the C^{13} and 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 P¹O⁶C⁵C⁴O⁷ cycle of the rigid bicycloheptane system of molecule 14 is a slightly distorted *envelope* [four-membered P¹O⁶C⁵C⁴ fragment is planar within 0.044(3) Å, and the O^7 atom deviates from the above fragment by -0.851(2) Å]. The O¹, O², O³, C³, C¹⁹, C²⁵ and C²⁶ 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) Å.

Considering that compounds 13 and 14 are formed simultaneously under very mild conditions (-40 °C) and the rearrangement of P–C-isomer 13 into P–O-isomer 14 is slow, it can

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be assumed that they are formed from the common unstable phosphorane intermediate 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 II, which finally results in the formation of compounds 13 and 14. The direction I, which includes P-O bond cleavage and the formation of intermediate bipolar ions B and C, is a kinetically controlled and reversible process. Direction II, which includes P-C bond cleavage and the formation of intermediate bipolar ions D and E, irreversibly results in a thermodynamically controlled reaction product, the P-Oisomer 14. Thus, the driving force of the PCO/POCrearrangements seems to be the greater thermodynamic stability of the resulting pentaalkoxyphosphorane 14 in comparison with its P-C-analogue 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 (C^4) formation occurred, two P-C diastereoisomers of isomer 13 should be formed. The formation of only one diastereoisomer indicates the high stereoselectivity of the second chiral center (C^4) 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 B. The very important fact that the relative configuration of the chiral C³ and C⁴ atoms in the P-C- and P-O-isomers 13 and 14, according to XRD data, is the same indicates the highly sternature of the intramolecular PCO/POCeoselective rearrangement.

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 (¹H, ¹³C and ¹⁹F 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 $O^1P^1O^3C^8$ fragment within 0.115(4) Å, and the C⁷ atom deviates from the abovementioned plane by -0.492(8) Å. The O^2 , C^9 and C^{12} atoms are located in axial positions (they deviate from the $O^1P^1O^3C^8$ plane by 1.574(5), -1.990(8) and 1.552(8) Å, respectively). The O^4 , C^{10} and C^{11} atoms are located in equatorial positions and deviate from the $O^1P^1O^3C^8$ plane by -0.851(4), 0.20(1) and -0.713(9) Å, respectively. Due to the presence of solvent water molecules in the crystal of 15, a classical hydrogen bond system is realized with the participation of the phosphoryl O^4 oxygen and water molecule protons $[O^{15}-H^{15}\cdots O^4]$.



Fig. 4 Geometry of molecule **15** in a crystal (solvate with water). Selected bond lengths (Å) and bond and torsion angles (°): P^1-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).

H^{1S}...O⁴ 2.0(1) Å, O^{1S}...O⁴ 2.75(1) Å, ∠O^{1S}-H^{1S}...O⁴ 178(8)°, and symmetry operation -1/2 + x, 1/2 - y, 1 - z] and also between hydrogen at the O² atom and water oxygen O^{1S} [O²-H²...O^{1S}interaction, the parameters are O²-H² 0.86(7) Å, H²...O^{1S} 1.61(7) Å, O²...O^{1S} 2.46(1) Å, ∠O²-H²...O^{1S} 168(9)°, 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 P–O-isomer 14 leads to the initial formation of dioxaphospholane 16. The ³¹P NMR spectrum of this compound contains a doublet (δ_P 11.0 ppm, ³ J_{PCCH} 5.9 Hz) with a coupling constant from the proton at C³, which indicates the retention of the P–O–C³ fragment. Its ¹³C 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 P¹–O² and P¹–O⁷ bonds in phosphorane 14 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 16 are presented in the ESI[†]). The phosphorus atom has a distorted tetrahedral configuration. The dioxaphospholane cycle has an *envelope* conformation with a planar four-membered $O^{1}P^{1}O^{3}C^{7}$ fragment within 0.080(6) Å, and the C⁸ atom deviates from this plane by 0.510(9) Å (see Fig. 7). The O^2 , C^{10} and C^{12} atoms are in axial positions (they deviate from the O¹P¹O³C⁸ plane by the values of 1.260(5), -1.52(1) and 2.05(1) Å, respectively). The O⁴, C⁹ and C¹¹ atoms are in equatorial positions (they deviate from the $O^1P^1O^3C^8$ plane by the values of -1.265(6), 0.74(1) and -0.05(1) Å, respectively). The presence of four methyl groups leads to a noticeable deviation of conformation along the C^7-C^8 bond from the regular staggered gauche conformation due to steric repulsion (the torsion angles C⁹C⁷C⁸C¹² and C¹⁰C⁷C⁸C¹¹ 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 ¹H and ¹³C spectra, and also by the different spin-spin coupling constants ${}^{3}J_{PCCC}$, which depend on the P–C–C–C torsion angle values. The same situation is realized for the conformation along the C^3-C^4 bond (the torsion angles of $O^2C^3C^4O^7$ and $C^{13}C^3C^4C^{16}$ 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 C³- C^4 bond (the torsion angle of $C^5C^4C^3C^{13}$ is $-166.7(7)^\circ$). Due to the classical hydrogen bond, $O^6-H^6...O^4$, the molecules of 16 are connected in dimers, and thus, a 0D supramolecular structure is realized in the crystal [the parameters of the



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 O⁶–H⁶ 0.66(6) Å, H⁶···O⁴ 2.14(6) Å, O⁶···O⁴ 2.76(1) Å, \angle O⁶–H⁶···O⁴ 155(7)°, 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 O⁷–H⁷···F¹ and O⁷–H⁷···O² classical hydrogen bonds [the parameters are O⁷–H⁷ 0.87(8) Å, H⁷···F¹ 2.34(9) Å, O⁷···F¹ 2.860(9) Å, \angle O⁷–H⁷···F¹ 119(8)°; and H⁷···O² 2.20(7) Å, O⁷···O² 2.722(8) Å, \angle O⁷–H⁷···O² 118(6)° respectively, see Fig. 8].

Prolonged hydrolysis of phosphorane 14 leads to the cleavage of not only the exocyclic P¹-O⁶ and P¹-O⁷ bonds but also the 1,3,2-dioxaphospholane P-O bonds. This process is accompanied by the formation of 2,3-dihydroxy-3trifluoromethyl-4,4,4-trifluoro-1,2-diphenylbutylphosphate 17 and pinacol. It should be noted that phosphate 17 ($\delta_{\rm P}$ – 1.4 ppm, $\delta_{\rm F}$ -67.05 and -67.82 ppm (CDCl₃/DMSO-d₆, 3 : 1)) exists in equilibrium with the cyclic form **19** ($\delta_{\rm P}$ 14.7 ppm (CD₃CN), $\delta_{\rm F}$ -68.42 and -69.98 ppm (CDCl₃/DMSO-d₆, 3 : 1)) (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 (40 $^{\circ}$ C) and the ratio becomes 2 : 1. Long crystallization of the hydrolysis products from CH2Cl2 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. 6 Geometry of molecule **16** in a crystal (racemate, $C_R^{3}C_5^{4}$ -enantiomer is shown). Selected bond lengths (Å) and bond and torsion angles (°): P^1-O^1 1.582(6), P^1-O^2 1.581(6), P^1-O^3 1.583(7), P^1-O^4 1.460(6), O^2-C^3 1.478(9), $O^1-P^1-O^2$ 101.2(3), $O^1-P^1-O^3$ 99.6(3), $O^1-P^1-O^4$ 118.9(4), $O^2-P^1-O^3$ 109.6(3), $O^2-P^1-O^4$ 112.7(3), $O^3-P^1-O^4$ 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 $O^2-C^3-C^4-O^7$ 46.1(8).



Fig. 8 The system of classical hydrogen bonds in the crystal of 16.



 $\ensuremath{\mathsf{Scheme}}$ 5 The equilibrium of phosphates 17 and 19 in dioxane solution.

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 $C_S{}^3C_R{}^4/C_R{}^3C_S{}^4$. The conformations of the monophosphate 17 and pinacol molecules along the C^4-C^3 , C^5-C^4 and C^6-C^{6a} 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 C^4-C^3 bond [the torsion angle of $C^{13}-C^3-C^4-C^{19}$ 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 (Å) and bond and torsion angles (°): P^1-O^1 1.535(5), P^1-O^2 1.588(4), P^1-O^3 1.551(4), P^1-O^4 1.489(4), $O^1-P^1-O^2$ 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), $O^2-P^1-O^4$ 111.3(2), $O^2-C^3-C^4-C^5$ 58.8(6), $P^1-O^2-C^3-C^4$ -168.4(3) and $C^3-C^4-C^5-C^{26}$ -163.4(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^{6a} (c) bonds.

The trifluoromethyl groups have different orientations relative to the phenyl ring at the C⁴ atom (see Fig. 10) and therefore fluorine atoms exhibit non-equivalence in the ¹⁹F NMR spectrum owing to the anisotropy of the phenyl ring.

Due to the classical O–H···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 O¹–H¹···O(4) interaction: O¹–H¹ 0.86(6) Å, H¹···O⁴ 1.76(6) Å, O¹···O⁴ 2.547(6) Å, $\angle O^1$ –H¹–O⁴ 152(9)°, and symmetry operation *x*, 3/2 – *y*, 1/2 + *z*; O³–H³···O⁵ 1.68(7) Å, $\angle O^3$ –H³···O⁵ 1.68(7) Å, H³···O⁵ 1.68(7) Å, O³···O⁵ 2.639(6) Å, $\angle O^3$ –H³–O⁵ 165(5)°, and symmetry operation –1 + *x*, 1 + *y*, –1 + *z*; O⁷–H⁷···O⁴ 1.85(7) Å, O⁷···O⁴ 2.802(6) Å, $\angle O^7$ –H⁷–O⁴ 159(8)°, 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 O⁷–H⁷–O⁴ 0.99(9) Å, H⁷····F¹ 2.31(9) Å, O⁷····F¹ 2.757(6) Å, and $\angle O^7$ –H⁷–P¹ 106(7)°, see ESI[†]].

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 g, 30 mmol) was condensed into a CCl₄/CH₂Cl₂ (1:1) solution (40 mL) of dioxaphosphole 12 (10.4 g, 30 mmol) at -40 °C. The reaction mixture was warmed up to 20 °C (10 h) and then evaporated under reduced pressure (14 Torr) to give a white precipitate of 13, which was filtered off and dried in vacuo (14 Torr). Yield 7.12 g (47%), mp 122-125 °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 °C). Clear white crystals of compound 13 were filtered off. Yield 3.62 g (24%), mp 123-125 °C. Anal. calcd for C₂₃H₂₃F₆O₅P (524.12): C, 52.68; H, 4.42; P, 5.91. Found: C, 52.63; H, 4.39; P, 5.98. IR (KBr) $(v_{\text{max}}, \text{ cm}^{-1})$: 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. ¹H NMR (400 MHz, CDCl₃)/ δ (ppm): 7.30 (m, 2H), 7.18 (m, 5H), 7.10 (m, 3H), 5.46 (d, 1H, ${}^{3}J_{POCH} = 17.0 \text{ Hz}, \text{H}^{3}$), 1.49 (br. s, 12H, CH₃). ${}^{13}\text{C}/{}^{13}\text{C}-\{^{1}\text{H}\}$ NMR (100.6 MHz, CDCl₃), (hereinafter a view of signal in ${}^{13}C-{}^{1}H$ NMR spectrum is in parentheses)/ $\delta_{\rm C}$ (ppm): 135.74 (m (d), ${}^{3}J_{\text{HCCC}} = 7.7 \text{ Hz}, {}^{2}J_{\text{HCC}} = 5.2 \text{ Hz}, {}^{3}J_{\text{POCC}} = 0.7 \text{ Hz}, \text{C}^{13}$, 133.36 (dt (d), ${}^{3}J_{POCC} = 12.2$ Hz, ${}^{3}J_{HCCC} = 7.5$ Hz, C¹⁹), 129.18 (dt (s), ${}^{1}J_{HC} =$ 160.7 Hz, ${}^{3}J_{\text{HCCC}} = 7.4$ Hz, C²²), 128.61 (dm (s), ${}^{1}J_{\text{HC}} = 161.0$ Hz, ${}^{3}J_{\text{HCCC}} = 7.2 \text{ Hz}, \text{C}^{16}$, 128.09 (br. dd (s), ${}^{1}J_{\text{HC}} = 160.3 \text{ Hz}, {}^{3}J_{\text{HCCC}}$ = 7.4 Hz, C^{15,17}), 127.90 (dd (s), ${}^{1}J_{HC}$ = 161.0 Hz, ${}^{3}J_{HCCC}$ = 7.0 Hz, $C^{21,23}$), 127.21 (br. ddd (s), ${}^{1}J_{HC} = 159.6$ Hz, ${}^{3}J_{HCCC} = 6.2-6.3$ Hz, ${}^{3}J_{\text{HCCC}} = 6.2-6.3$ Hz, $C^{14,18}$), 125.82 (ddd (s), ${}^{1}J_{\text{HC}} = 161.1$ Hz, ${}^{3}J_{\text{HCCC}} = 7.4 \text{ Hz}, {}^{3}J_{\text{HCCC}} = 6.2 \text{ Hz}, \text{C}^{20,24}$), 122.60 (qd (qd), ${}^{1}J_{\text{FC}} =$ 285.8 Hz, ${}^{2}J_{PCC} = 1.1$ Hz, C²⁶), 121.71 (br. qd (qd), ${}^{1}J_{FC} = 289.8$ Hz, ${}^{2}J_{PCC} = 5.7$ Hz, C²⁵), 99.76 (ddm (d), ${}^{2}J_{POC} = 23.9$ Hz, ${}^{2}J_{HCC} =$ 4.2-4.4 Hz, ${}^{3}J_{HCCC} =$ 4.2-4.4 Hz, C⁴), 87.68 (dmd (d), ${}^{1}J_{HC} =$ 156.3 Hz, ${}^{2}J_{POC} = 2.9$ Hz, ${}^{3}J_{HCCC} = 4.4$ Hz, C³), 82.93 (m (d), ${}^{2}J_{POC}$ = 2.2 Hz, ${}^{2}J_{HCC}$ = 4.2–4.4 Hz, $C_{eq.}{}^{8}$), 79.17 (m (d), ${}^{2}J_{POC}$ = 2.9 Hz, ${}^{2}J_{\text{HCC}} = 4.4$ Hz, $C_{\text{ax}}{}^{7}$), 77.78 (d. sept (d. sept), ${}^{1}J_{\text{PC}} = 154.8$ Hz,

 ${}^{2}J_{FCC} = 30.7$ Hz, C⁶), 23.52 (br. qdq (br. d), ${}^{1}J_{HC} = 127.3$ Hz, ${}^{3}J_{POCC} = 11.0$ Hz, ${}^{3}J_{HCCC} = 4.0$ Hz, C⁹⁻¹²). 19 F NMR (376.5 MHz, CDCl₃)/ $\delta_{\rm F}$ (ppm): -68.44 (q. d, ${}^{4}J_{FCCCF} = 10.3$ Hz, ${}^{3}J_{PCCF} = 4.6$ Hz), -68.87 (q, ${}^{4}J_{FCCCF} = 10.3$ Hz, ${}^{3}J_{PCCF} = 2.3$ Hz). 31 P-{ 1 H}/ 31 P NMR (161.9 MHz, CDCl₃)/ $\delta_{\rm P}$ (ppm): -25.1 (dd (s), ${}^{3}J_{PCCH} = 17.6$ Hz, ${}^{3}J_{PCCF} = 1.9$ Hz). ESI-MS (*m*/*z*): 523.97.

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

A mixture of compound 13 (6.00 g, 11.45 mmol) and CH₂Cl₂ (20 mL) was kept for five days (control by ³¹P 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 (-18 °C). The crystalline precipitate of 14 was filtered off and dried in vacuo (14 Torr). Yield 5.34 g (89%), mp 125-127 °C. Anal. calcd for C₂₃H₂₃F₆O₅P (524.12): C, 52.68; H, 4.42; P, 5.91. Found: C, 52.64; H, 4.40; P, 5.93. IR (KBr) (ν_{max} , 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. ¹H NMR (400 MHz, CDCl₃)/ δ (ppm): 7.44 (m, 1H), 7.30 (m, 1H), 7.17 (m, 3H), 7.08 (m, 5H), 5.72 (d, 1H, ${}^{3}J_{POCH} = 19.2$ Hz, H³), 1.52 (s, 3H, CH₃), 1.51 (s, 3H, CH₃), 1.43 (s, 3H, CH₃), 1.38 (s, 3H, CH₃). ${}^{13}C/{}^{13}C-{}^{1}H$ NMR (100.6 MHz, CDCl₃)/ δ_{C} (ppm): 135.40 (tt (s), ${}^{3}J_{HCCC} = 5.1-5.3$ Hz, ${}^{2}J_{HCC} = 2.2$ Hz, C¹³), 131.08 (dt (d), ${}^{3}J_{POCC} = 18.7$ Hz, ${}^{3}J_{HCCC} = 7.2$ Hz, C¹⁹), 128.59 (dm (s), ${}^{1}J_{\text{HC}} = 160.7 \text{ Hz}, {}^{3}J_{\text{HCCC}} = 7.3 \text{ Hz}, {}^{3}J_{\text{HCCC}} = 7.3 \text{ Hz}, \text{ C}^{16} \text{ or } \text{C}^{22}$), 128.56 (dm (s), ${}^{1}J_{HC} = 160.7$ Hz, ${}^{3}J_{HCCC} = 7.3$ Hz, ${}^{3}J_{HCCC} = 7.3$ Hz, C^{16} or C^{22}), 128.52 (dm (s), ${}^{1}J_{HC} = 161.4$ Hz, ${}^{3}J_{HCCC} = 7.3$ Hz, ${}^{3}J_{\rm HCCC}$ = 7.3 Hz, C^{14,18}), 127.98 (br. dd (s), ${}^{1}J_{\rm HC}$ = 160.5 Hz, ${}^{3}J_{\text{HCCC}} = 7.2 \text{ Hz}, \text{ C}^{23}$), 127.93 (br. dm (br. sept), ${}^{1}J_{\text{HC}} = 160.5 \text{ Hz}$, ${}^{5}J_{\text{FCCCCC}} = 1.9 \text{ Hz}, \text{C}^{24}$), 127.76 (dm (s), ${}^{1}J_{\text{HC}} = 160.7 \text{ Hz}, {}^{3}J_{\text{HCCC}} =$ 6.0–7.0 Hz, $C^{15,17}$), 127.13 (br. dd (s), ${}^{1}J_{HC} = 161.4$ Hz, ${}^{3}J_{HCCC} =$ 7.3 Hz, C^{21}), 126.90 br. dm (br. q), ${}^{1}J_{HC} = 160.5$ Hz, ${}^{5}J_{FCCCCC} =$ 5.0 Hz, C^{20}), 122.40 (qd (qd), ${}^{1}J_{FC} = 286.4$ Hz, ${}^{3}J_{POCC} = 8.6$ Hz, CF₃), 121.08 (qd (qd), ${}^{1}J_{FC} = 289.4$ Hz, ${}^{3}J_{POCC} = 2.7$ Hz, CF₃), 83.41 (sept (sept), ${}^{2}J_{CCF} = 29.3$ Hz, C⁵), 82.93 (m (d), ${}^{2}J_{POC} = 2.2$ Hz, ${}^{2}J_{HCC} = 3.6$ Hz, ${}^{3}J_{HCCC} = 3.8$ Hz, C_{eq} .⁷), 82.47 (dm (dq), ${}^{1}J_{HC}$ = 154.8 Hz, ${}^{2}J_{POC}$ = 2.9 Hz, ${}^{4}J_{FCCCC}$ = 2.6–2.8 Hz, C³), 79.74 (dt (d), $^2\!J_{\rm POC} = 20.2$ Hz, $^3\!J_{\rm HCCC} = 3.7$ Hz, C^4), 79.30 (m (d), $^2\!J_{\rm POC} =$ 2.9 Hz, ${}^{2}J_{HCC} = 3.7$ Hz, ${}^{3}J_{HCCC} = 3.6-3.7$ Hz, C_{ax}^{8}), 23.72 (qdq (d), ${}^{1}J_{\text{HC}} = 127.6 \text{ Hz}, {}^{3}J_{\text{POCC}} = 6.2 \text{ Hz}, {}^{3}J_{\text{HCCC}} = 4.4 \text{ Hz}, C^{9}-C_{\text{eq.}}^{7}$ 23.69 (qdq (d), ${}^{1}J_{HC} = 127.6$ Hz, ${}^{3}J_{POCC} = 5.2$ Hz, ${}^{3}J_{HCCC} = 4.4$ Hz, $C^{10}-C_{eq.}^{7}$), 23.54 (qdq (d), ${}^{1}J_{HC} = 127.5$ Hz, ${}^{3}J_{POCC} = 7.7$ Hz, ${}^{3}J_{\text{HCCC}} = 4.4$ Hz, C^{11} - $C_{ax}{}^{8}$), 23.36 (qdq (d), ${}^{1}J_{\text{HC}} = 127.5$ Hz, ${}^{3}J_{POCC} = 8.0$ Hz, ${}^{3}J_{HCCC} = 4.4$ Hz, $C^{12}-C_{ax}^{8}$). ${}^{19}F$ NMR (376.5) MHz, CDCl₃) $/\delta_{\rm F}$ (ppm): -68.22 (q, ${}^{4}J_{\rm FCCCF} = 9.5$ Hz), -72.35 (q, ${}^{4}J_{\text{FCCCF}} = 9.5 \text{ Hz}$). ${}^{31}\text{P} - \{{}^{1}\text{H}\}/{}^{31}\text{P}$ NMR (161.9 MHz, CDCl₃)/ δ_{P} (ppm): -27.3 (d (s), ${}^{3}J_{POCH} = 20.4$ Hz). ESI-MS (*m*/*z*): 523.97.

Hydrolysis of compound 13

To a suspension of compound **13** (1 g, 1.91 mmol) in diethyl ester (5 mL), a solution of 0.1 mL (5.72 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 H₂O molecule) was filtered off and dried in vacuo (14 Torr). Yield 0.31 g (83%), mp 190–192 °C. ¹H NMR (400 MHz, DMF- d_7), δ : 8.72 (br. s, 1H, OH), 1.41 (br. s, 12H, H⁹⁻¹²). ³¹P-{¹H} NMR (161.9 MHz, DMF- d_7), δ_P : 10.6 ppm (s). The ¹H 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 (¹H, ¹³C, ¹⁹F NMR) with previously published data.43 The filtrate was evaporated in vacuo (14 Torr) to give a white precipitate of benzoin, mp 132–134 °C. ¹H NMR (600.0 MHz, acetone- d_6 /CDCl₃ = 2 : 1)/ δ (ppm): 8.03 (m, 2H, XX'-part of AA'XX'-subsystem, ${}^{3}J_{AX} = {}^{3}J_{A'X'} = 7.5$ Hz, H^{20,24}), 7.56 (tt, 1H, ${}^{3}J_{AM}$ $= {}^{3}J_{A'M} = 7.5$ Hz, ${}^{4}J_{XM} = {}^{4}J_{X'M'} = 1.5$ Hz, *M*-part of *AA'MXX'*system, H²²), 7.45 (br. dd, 2H, AA'-part of AA'XX'-subsystem, ³J_{AX} $={}^{3}J_{A'X'}=7.5$ Hz, ${}^{3}J_{AM}={}^{3}J_{A'M'}=7.5$ Hz, H^{21,23}), 7.44 (m, 2H, XX'part of AMM'XX'-system, ${}^{3}J_{XM} = {}^{3}J_{X'M'} = 7.5$ Hz, H^{14,18}), 7.32 (br dd, 2H, *MM'*-part of *AMM'XX'*-system, ${}^{3}J_{XM} = {}^{3}J_{X'M'} = 7.5$ Hz, ${}^{3}J_{AM}$ $= {}^{3}J_{AM'} = 7.5$ Hz, H^{15,17}), 7.25 (tt, 1H, A-part of AMM'XX'-system, ${}^{3}J_{AM} = {}^{3}J_{AM'} = 7.5 \text{ Hz}, \, {}^{4}J_{AX} = {}^{4}J_{AX'} = 1.5 \text{ Hz}, \text{H}^{16}$), 6.13 (s, 1H, H³), 4.93 (br. s, 1H, OH). ¹³C/¹³C-{¹H} NMR (150.0 MHz, acetone-*d*₆/ $\text{CDCl}_3 = 2:1)/\delta_{\text{C}}$ (ppm): 200.01 (br. dt (s), ${}^2J_{\text{HC}^3\text{C}^4} = 3.5$ Hz, ${}^{3}J_{\text{HC}^{20,24}\text{CC}^{4}} = 3.3 \text{ Hz}, \text{ C}^{4}$, 140.75 (tdd (s), ${}^{3}J_{\text{HC}^{15,17}\text{CC}^{13}} = 7.5 \text{ Hz}$, ${}^{2}J_{\text{HC}^{3}\text{C}^{13}} = 5.5$ Hz, ${}^{3}J_{\text{HOCC}^{13}} = 1.3$ Hz, C¹³), 135.36 (br. t (s), ${}^{3}J_{\rm HC^{21,23}CC^{19}} =$ 7.4 Hz, C¹⁹), 134.27 (dt (s), ${}^{1}J_{\rm HC^{22}} =$ 162.9 Hz, ${}^{3}J_{\text{HC}^{20,24}\text{CC}^{22}} = 7.7 \text{ Hz}, \text{ C}^{22}$, 129.86 (ddddd (s), ${}^{1}J_{\text{HC}^{20,24}} = 161.3 \text{ Hz},$ ${}^{3}J_{\text{HC}^{24,20}\text{CC}^{20,24}} = 7.6 \text{ Hz}, {}^{3}J_{\text{HC}^{22}\text{CC}^{20,24}} = 7.6 \text{ Hz}, {}^{2}J_{\text{HC}^{21,23}\text{C}^{20,24}} = 1.7 \text{ Hz},$ ${}^{4}J_{\mathrm{HC}^{4}\mathrm{CCC}^{20,24}} = 1.3 \text{ Hz}, \mathrm{C}^{20,24}$), 129.52 (br. dm (s), ${}^{1}J_{\mathrm{HC}^{15,17}} = 161.5 - 1000 \text{ J}_{\mathrm{HC}^{10}}$ 161.8 Hz, ${}^{3}J_{\text{HC}^{15,17}\text{CC}^{17,15}} = 6.0-7.0$ Hz, C^{15,17}), 129.41 (dd (s), ${}^{1}J_{\text{HC}^{21,23}} = 161.7 \text{ Hz}, {}^{3}J_{\text{HC}^{23,21}\text{CC}^{21,23}} = 7.6 \text{ Hz}, \text{C}^{21,23}$, 128.84 (dtd (s), ${}^{1}J_{\text{HC}^{16}} = 161.0 \text{ Hz}, {}^{3}J_{\text{HC}^{14,18}\text{CC}^{16}} = 7.6 \text{ Hz}, {}^{5}J_{\text{HC}^{3}\text{CCCC}^{16}} = 1.1 \text{ Hz}, \text{C}^{16}),$ 128.44 (dm (s), ${}^{1}J_{HC^{14,18}} = 162.4$ Hz, ${}^{3}J_{HC^{18,14}CC^{14,18}} = 6.5-7.5$ Hz, ${}^{3}J_{\mathrm{HC}^{16}\mathrm{CC}^{14,18}} = 6.5-7.5 \mathrm{Hz}, {}^{3}J_{\mathrm{HC}^{3}\mathrm{CC}^{14,18}} = 4.5 \mathrm{Hz}, \mathrm{C}^{14,18}$, 76.94 (dt (s), ${}^{1}J_{\text{HC}^{3}} = 146.8 \text{ Hz}, {}^{3}J_{\text{HC}^{14,18}\text{CC}^{3}} = 4.0 \text{ Hz}, \text{ C}^{3}$). ${}^{13}\text{C}-\{{}^{1}\text{H}\}$ NMR (100.6 MHz, CDCl₃), $\delta_{\rm C}$: 199.15 (br. dt (s), ${}^{2}J_{\rm HC^{3}C^{4}} = 3.3$ Hz, ${}^{3}J_{\rm HC^{20,24}CC^{4}} =$ 3.3 Hz, C⁴), 139.20 (tdd (s), ${}^{3}J_{\text{HC}^{15,17}\text{CC}^{13}} = 7.3$ Hz, ${}^{2}J_{\text{HC}^{3}\text{C}^{13}} = 5.5$ Hz, ${}^{3}J_{\text{HOCC}^{13}} = 2.2 \text{ Hz}, \text{C}^{13}$, 133.74 (br. t (s), ${}^{3}J_{\text{HC}^{21,23}\text{CC}^{19}} = 7.7 \text{ Hz}, \text{C}^{19}$), 134.07 (br. td (s), ${}^{1}J_{HC^{22}} = 162.2$ Hz, ${}^{3}J_{HC^{20,24}CC^{22}} = 7.7$ Hz, C^{22}), 129.33 (ddddd (s), ${}^{1}J_{HC^{20,24}} = 160.7$ Hz, ${}^{3}J_{HC^{24,20}CC^{20,24}} = 7.6$ Hz, ${}^{3}J_{\text{HC}^{22}\text{CC}^{20,24}} = 7.6 \text{ Hz}, {}^{2}J_{\text{HC}^{21,23}\text{C}^{20,24}} = 1.4 \text{ Hz}, {}^{4}J_{\text{HC}^{4}\text{CCC}^{20,24}} = 1.2 \text{ Hz},$ $C^{20,24}$), 129.30 (br. dd (s), ${}^{1}J_{HC^{15,17}} = 161.0$ Hz, ${}^{3}J_{HC^{15,17}CC^{17,15}} = 6.5-$ 7.0 Hz, $C^{15,17}$), 128.86 (dd (s), ${}^{1}J_{HC^{21,23}} = 162.5$ Hz, ${}^{3}J_{HC^{23,21}CC^{21,23}} =$ 7.7 Hz, $C^{21,23}$), 128.76 (dtt (s), ${}^{1}J_{HC^{16}} = 161.0$ Hz, ${}^{3}J_{HC^{14,18}CC^{16}} = 7.2$ Hz, ${}^{2}J_{HC^{15,17}C^{16}} = 1.5$ Hz, C¹⁶), 127.96 (dm (s), ${}^{1}J_{HC^{14,18}} = 162.4$ Hz, ${}^{3}J_{\rm HC^{18,14}CC^{14,18}} = 6.5-7.5 \text{ Hz}, \, {}^{3}J_{\rm HC^{16}CC^{14,18}} = 6.5-7.5 \text{ Hz}, \, {}^{3}J_{\rm HC^{3}CC^{14,18}} =$ 4.5 Hz, $C^{14,18}$), 76.42 (dtd (s), ${}^{1}J_{HC^{3}} = 146.8$ Hz, ${}^{3}J_{HC^{14,18}CC^{3}} = 3.4$ Hz, ${}^{2}J_{\text{HOC}^{3}} = 1.5$ Hz, C³).

Hydrolysis of compound 14

To a suspension of compound **14** (3.54 g, 6.75 mmol) in 10 mL of diethyl ester, a solution of 0.12 mL (6.75 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 °C. Anal. calcd for $C_{23}H_{25}F_6O_6P$ (542.41): C, 50.93; H, 4.65; P, 5.71. Found: C, 50.94; H, 4.60; P, 5.73. IR (nujol) (ν_{max} , 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. ¹H NMR (400 MHz, DMF-*d*₇)/ δ (ppm): 8.74 (br. s, 1H, OH), 7.60 (d, 2H, ${}^{3}J_{\text{HCCH}}$ 5.6 Hz, H^{20,24}), 7.23 (m, 2H, ${}^{3}J_{\text{HCCH}} = 6.7-7.7 \text{ Hz}$, ${}^{5}J_{\text{PCCCCH}} = 1.5 \text{ Hz}$, $\mathrm{H}^{14,18}$), 7.11 (m, 3H, H^{21-23}), 7.05 (m, 3H, H^{15-17}), 6.25 (d, 1H, ${}^{3}J_{POCH} = 7.6$ Hz, H³), 5.98 (s, 1H, OH), 1.49 (s, 3H, Me), 1.42 (s, 6H, Me), 1.26 (s, 3H, Me). ${}^{13}C/{}^{13}C-{}^{1}H$ NMR (100.6 MHz, DMF- d_7)/ δ_C (ppm): 139.45 (br. td (br. s), ${}^{3}J_{HCCC} = 6.2$, ${}^{2}J_{HCC} = 5.2$, C¹³), 138.09 (ddd (s), ${}^{3}J_{HCCC} = 7.2$ Hz, ${}^{3}J_{HCCC} = 6.7$ Hz, ${}^{3}J_{HCCC} = 3.7$ Hz, C^{19}), 130.91 (dddd (s), ${}^{1}J_{HC} = 163.3 \text{ Hz}, {}^{3}J_{HCCC} = 5.4 \text{ Hz}, {}^{3}J_{HCCC} = 5.2$ Hz, ${}^{3}J_{\text{HCCC}} = 5.2$ Hz, $C^{14,18}$), ~129.2 (v. br. d (v. br. s) C^{20}), 128.53 $(dt (s), {}^{1}J_{HC} = 160.0 \text{ Hz}, {}^{3}J_{HCCC} = 7.4 \text{ Hz}, C^{16}), 128.13 (dt (s), {}^{1}J_{HC})$ = 160.0 Hz, ${}^{3}J_{\text{HCCC}} = 7.7$ Hz, C²²), 127.69 (br. dd (s), ${}^{1}J_{\text{HC}} = 161.8$ Hz, ${}^{3}J_{\text{HCCC}} = 5.0-6.0$ Hz, C^{15,17}), 127.37 (v. br. d (v. br. s), ${}^{1}J_{\text{HC}}$ ~160.0–162.0 Hz, $C^{21,23,24}$), 124.80 (q (q), ${}^{1}J_{FC} = 291.6$ Hz, CF_{3}), 124.58 (q (q), ${}^{1}J_{FC} = 291.1$ Hz, CF₃), 89.33 (m (d), ${}^{2}J_{POC} = 1.2$ Hz, C^{7} or C^{8}), 89.23 (m (s), C^{8} or C^{7}), 83.34 (sept (sept), ${}^{2}J_{FCC} = 25.6$ Hz, C⁵), 82.89 (br. dm (br. d), ${}^{1}J_{HC} = 149.5$ Hz, ${}^{2}J_{POC} = 5.1$ Hz, C^{3}), 81.75 (br. d (d), ${}^{3}J_{POCC} = 10.0$ Hz, C^{4}), 24.76, 24.27, 24.14 and 23.97 ppm (four qdq (four d), ${}^{1}J_{HC} = 127.5, 127.5, 127.8$ and 127.9 Hz, ${}^{3}J_{POCC} = 4.4$, 7.0, 3.9 and 6.5 Hz, ${}^{3}J_{HCCC} = 4.3-4.4$ Hz, C^{9-12}). ¹⁹F NMR (376.4 MHz, DMF- d_7)/ δ_F (ppm): -67.43 (q, ${}^{4}J_{\text{FCCCF}} = 11.3 \text{ Hz}$, -68.19 (q, ${}^{4}J_{\text{FCCCF}} = 11.3 \text{ Hz}$). ${}^{31}\text{P}/{}^{31}\text{P}-\{{}^{1}\text{H}\}$ NMR (161.9 MHz, DMF- d_7)/ δ_P (ppm): 11.0 (d (s), ${}^{3}J_{PCCH} = 5.9$ Hz). ${}^{13}C/{}^{13}C-{}^{1}H$ NMR (100.6 MHz, DMSO- d_6)/ δ_C (ppm): 139.45 (br. td (br. s), C^{13}), 137.0 (m (s), C^{19}), 129.63 (dddd (s), ${}^{1}J_{HCCC} =$ 160.0 Hz, ${}^{3}J_{\text{HCCC}} = 6.0-7.0$ Hz, ${}^{3}J_{\text{HCCC}} = 6.0-7.0$ Hz, ${}^{3}J_{\text{HCCC}} = 4.4$ Hz, $C^{14,18}$), ~129.2 (v. br. d (v. br. s) C^{20}), 127.65 (dt (s), ${}^{1}J_{HC} =$ 160.0 Hz, ${}^{3}J_{\text{HCCC}} = 7.3$ Hz, C¹⁶), 127.28 (dt (s), ${}^{1}J_{\text{HC}} = 160.0$ Hz, ${}^{3}J_{\text{HCCC}} = 7.7 \text{ Hz}, \text{ C}^{22}$), 126.81 (dd (s), ${}^{1}J_{\text{HC}} = 160.0 \text{ Hz}, {}^{3}J_{\text{HCCC}} =$ 6.6 Hz, $C^{15,17}$), ~126.9 (v. br. d (v. br. s), ${}^{1}J_{HC}$ ~160.0–162.0 Hz, $C^{21,23,24}$), 124.68 (q (q), ${}^{1}J_{FC} = 292.0$ Hz, CF_{3}), 123.45 (q (q), ${}^{1}J_{FC}$ = 290.5 Hz, CF₃), 89.31 (m (s), C⁷ or C⁸), 88.18 (m (s), C⁸ or C⁷), 82.01 (sept (sept), ${}^{2}J_{FCC} = 25.6$ Hz, C⁵), 81.29 (br. dm (br. d), ${}^{1}J_{HC}$ = 149.0 Hz, ${}^{2}J_{POC}$ = 4.8 Hz, C³), 80.59 (br. d (d), ${}^{3}J_{POCC}$ = 9.9 Hz, C^4), 24.24, 23.72, 23.55 and 23.37 (four qdq (four d), ${}^1J_{HC} =$ 127.6, 127.6, 128.4 and 129.1 Hz, ${}^{3}\!J_{\rm POCC} =$ 3.7, 7.0, 3.3 and 6.2 Hz, ${}^{3}J_{\text{HCCC}} = 3.0-3.3$ Hz, C⁹⁻¹²). 19 F NMR (376.4 MHz, DMSO- d_{6})/ $\delta_{\rm F}$ (ppm): -66.49 (br. q, ${}^{4}J_{\rm FCCCF}$ = 10.9 Hz), -68.10 (br. q, ${}^{4}J_{\rm FCCCF}$ = 10.9 Hz). ${}^{31}P/{}^{31}P-{}^{1}H$ NMR (161.9 MHz, DMSO- d_6)/ δ_P (ppm): 10.7 (d (s), ${}^{3}J_{PCCH} = 7.8$ Hz). MALDI-MS (m/z): 565.03 (M + Na), 580.93 (M + K).

Hydrolysis of compound 16

Compound **16** (1.50 g, 2.77 mmol) was refluxed in a solution (15 mL) of dioxane and H₂O (2 : 1) for 20 hours (control by ³¹P NMR). ³¹P/³¹P-{¹H} NMR (161.9 MHz, dioxane/ $\delta_{\rm P}$ (ppm): -1.2 (d (s), ³J_{PCCH} = 5.6 Hz), 14.0 (br. s (s)). ¹⁹F NMR (376.4 MHz, CDCl₃)/ $\delta_{\rm F}$ (ppm): -67.39 (q, ⁴J_{FCCCF} = 10.9 Hz), -68.65 (q, ⁴J_{FCCCF} = 10.9 Hz), -68.65 (q, ⁴J_{FCCCF} = 9.5 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 CH₂Cl₂ (10 mL). The crystalline precipitate of **18** (adduct with pinacol) was filtered off and dried *in vacuo* (14 Torr). Yield 1.01 g (63%), mp 99–103 °C. Anal. calcd for C₂₃H₂₉F₆O₈P (578.44): C, 47.76; H, 5.05; P, 5.35.

Found: C, 47.74; H, 5.00; P, 5.31. IR (nujol) (*v*_{max}, cm⁻¹): 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. ¹H NMR (400 MHz, CD_3CN / δ (ppm): 7.46 (br. d, 2H, H^{20,24}), 7.21 (d, ${}^{3}J_{HCCH} = 7.1$ Hz, 2H, H^{14,18}), 7.10 (m, 3H, H^{19,20,21}), 7.04 (m, 3H, H^{15,16,17}), 6.09 (d, ${}^{3}J_{POCH} = 4.9$ Hz, 1H, H³), 1.16 (s, 12H, Me, pinacol). $^{13}C/^{13}C-\{^{1}H\}$ NMR (100.6 MHz, CD₃CN)/ δ_{C} (ppm): 137.98 (br. td (s), ${}^{2}J_{HCC} = 5.5$, C¹⁹), 137.07 (br. td (br. s), ${}^{3}J_{HCCC}$ 7.3 Hz, C¹³), 131.10 (br. d (s), ${}^{1}J_{\text{HCCC}} = 156.6 \text{ Hz}, \text{C}^{14,18}$), ~127.9 (v. br. d (v. br. s) C^{20,24}), 128.71 (br. dt (s), ¹J_{HC} 161.4 Hz, C¹⁶), 128.64 (br. dt (s), ${}^{1}J_{\text{HC}}$ 161.7 Hz, C²²), 128.10 (br. dd (s), ${}^{1}J_{\text{HC}}$ = 158.5 Hz, ${}^{3}J_{\text{HCCC}}$ = 7.3 Hz, C^{15,17}), 127.85 and 126.74 (two v. br. d (two v. br. s), C^{20,24} and $C^{21,23}$), 124.35 (q (q), ${}^{1}J_{FC} = 289.4$ Hz, CF_{3}), 124.18 (q (q), ${}^{1}J_{FC}$ = 290.9 Hz, CF₃), 90.34 (m (s), pinacol), 83.79 (sept (sept), ${}^{2}J_{FCC}$ = 25.7 Hz, C^5), 83.12 (d. m (d), ${}^{1}J_{HC}$ = 151.5 Hz, ${}^{2}J_{POC}$ = 2.6 Hz, C^{3}), 81.87 (m (d), ${}^{3}J_{POCC} = 8.1 \text{ Hz}, C^{4}$), 25.16 (q (s), ${}^{1}J_{HC} = 125.4$, CH₃, pinacol). ¹⁹F NMR (376.4 MHz, CDCl₃/DMSO- d_6 (3 : 1))/ δ_F (ppm): -67.05 (q, ${}^{4}J_{FCCCF} = 11.2$ Hz), -67.82 (q, ${}^{4}J_{FCCCF} = 10.2$ Hz). ${}^{31}P/{}^{31}P-{}^{1}H$ NMR (161.9 MHz, CD₃CN)/ δ_P (ppm): -1.4 (br. 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 MoK_{α} (0.71073 Å) radiation and ω 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 SHELX⁴⁸ program. All crystal structure pictures were created using Mercury CSD 2.4.⁴⁹

Crystal data for 13

 $C_{23}H_{23}F_6O_5P$, M = 524.38, monoclinic, a = 9.485(6), b = 11.002(7), c = 12.115(8) Å, $\beta = 101.517(8)^\circ$, V = 1239(1) Å³, T = 296 K, space group $P2_1$ (no. 4), Z = 2, 12 827 reflections measured, 4529 unique ($R^{int} = 0.071$), which were used in all calculations. Final indices $R_1 = 0.0667$, $wR_2 = 0.1629$ for 2921 reflections with $I > 2\sigma(I)$; $R_1 = 0.1100$, $wR_2 = 0.2021$ for all data.

Crystal data for 14

 $C_{23}H_{23}F_6O_5P$, M = 524.38, orthorhombic, a = 12.650(5), b = 16.695(6), c = 22.988(9) Å, V = 4855(3) Å³, T = 296 K, space group *Pbca* (no. 61), Z = 8, 28 292 reflections measured, 4766 unique ($R^{int} = 0.066$), which were used in all calculations. Final indices $R_1 = 0.0520$, w $R_2 = 0.1426$ for 2856 reflections with $I > 2\sigma(I)$; $R_1 = 0.0985$, w $R_2 = 0.1825$ for all data.

Crystal data for 15

C₆H₁₅O₅P, M = 198.15, orthorhombic, a = 6.39(2), b = 10.62(3), c = 14.67(3) Å, V = 995(4) Å³, T = 296 K, space group $P2_12_12_1$ (no. 19), Z = 4, 5025 reflections measured, 1949 unique ($R^{int} = 0.068$), which were used in all calculations. Final indices $R_1 =$

0.0499, w $R_2 = 0.1437$ for 1316 reflections with $I > 2\sigma(I)$; $R_1 = 0.0907$, w $R_2 = 0.1841$ for all data.

Crystal data for 16

C₂₃H₂₅F₆O₆P, M = 542.40, triclinic, a = 10.788(13), b = 10.889(13), c = 12.329(15) Å, $\alpha = 70.63(2)$, $\beta = 71.74(2)$, $\gamma = 67.88(2)^{\circ}$, V = 1236(3) Å³, T = 296 K, space group $P\bar{1}$ (no. 2), Z = 2, 4706 reflections measured, which were used in all calculations. Final indices $R_1 = 0.0880$, w $R_2 = 0.2734$ for 2147 reflections with $I > 2\sigma(I)$; $R_1 = 0.1946$, w $R_2 = 0.3522$ for all data.

Crystal data for 18

 $C_{17}H_{15}F_6O_6P \quad 0.5C_6H_{14}O_2, M = 519.34, \text{monoclinic}, a = 18.721(8), b = 13.944(6), c = 8.706(4) Å, \beta = 95.489(8)^\circ, V = 2262(2) Å^3, T = 296 K, \text{space group } P2_1/c \text{ (no. 14)}, Z = 4, 11 470 \text{ reflections measured}, 4448 unique (<math>R^{\text{int}} = 0.152$), which were used in all calculations. Final indices $R_1 = 0.0773$, $wR_2 = 0.1632$ for 1683 reflections with $I > 2\sigma(I)$; $R_1 = 0.2229$, $wR_2 = 0.2372$ 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 (P-C/P-O)-phosphoranes 13 and 14 in the ratio of 10:1. In dichloromethane solution (20 °C, 5 days), the rearrangement of P-C-isomer 13 to P-O-isomer 14 proceeds with high stereoselectivity (>96%). The P-C-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 P-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 C^3 and C^4 atoms, and further hydrolysis of this compound yields 2,3-dihydroxy-3trifluoromethyl-4,4,4-trifluoro-1,2-diphenyl butylphosphate 17 and pinacol.

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