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-1,2-diphenylethoxy)-1,3,2-dioxaphospholane and hexafluoroacetone†

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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 Appel15,16 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(III)-derivatives to unsaturated systems, various reactions of tetracoordinated phosphorus and substitution reactions at P(V)19,29 should be noted.

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.28–34 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=O-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.29–32

Scheme 2 demonstrates the synthetic potential of the intramolecular cascade cyclization of P(III)-derivatives 1 under the
action of prochiral trifluoropyruvic acid ethyl ester and chloral, which allows the P-C-cage phosphoranes 5–8 to be obtained with high stereoselectivity.35,36

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[III] atom in the dioxaphospholane cycle results in the simultaneous formation of PCO- and POC-isomers (1:1) of cage phosphoranes10,11 in the reaction of 4,5-dimethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane8 with hexafluoroacetic acid (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-hydroxalkylphosphonates (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,18 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 (CCl₄, −40 °C) with the simultaneous formation of two isomeric pentacoordinated phosphorus species 13 and 14 (Scheme 4), which have two high-field signals at δₚ = −24.5 and δₚ = −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, δₚ = −25.1 ppm, ³¹FCCCF = 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[2.2.1.1⁰⁰]heptane. The ¹³F NMR spectrum contains two signals at δF = −68.48 (qd, ³¹FCCCF = 10.3 Hz, ³¹FCCCF = 4.6 Hz) and δF = −68.94 ppm (qd, ³¹FCCCF = 10.3 Hz, ³¹FCCCF = 2.3 Hz) with an equal integral intensity, which correspond to the non-equivalent fluorine atoms of CF₃-groups. In contrast to the abovementioned phosphorane 9, which is a hexafluoroaceton 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 P₃/O₃/C₆/C₆. A small deviation in the phosphorus atom from the O₃O₂O₆ 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, O₁, 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 1−P₁−O₇ is equal to 172.4

![Scheme 2](image1)

**Scheme 2** Reaction of P(α)-derivatives 1 bearing an exocyclic C=O bond with trifluoropyruvic acid ethyl ester and chloral.

![Scheme 3](image2)

**Scheme 3** Simultaneous formation of PCO- and POC-isomers 10 and 11 in the reaction of phospholane 1 with hexafluoroacetone.
One of the two trifluoromethyl groups (C\textsubscript{2}F\textsubscript{3}) is almost in this plane [C\textsubscript{25} atom deviation from it is 0.21(1) Å]. The O\textsuperscript{1}–P\textsuperscript{1}–O\textsuperscript{1}, O\textsuperscript{1}–P\textsuperscript{1}–O\textsuperscript{5}, O\textsuperscript{1}–P\textsuperscript{1}–C\textsubscript{6}, O\textsuperscript{2}–P\textsuperscript{1}–O\textsuperscript{7} and O\textsuperscript{2}–P\textsuperscript{1}–C\textsubscript{6} bond angles vary within the limits of 83.3(3)–96.9(3)°. The O\textsuperscript{2}–P\textsuperscript{1}–C\textsubscript{6}, O\textsuperscript{2}–P\textsuperscript{1}–O\textsuperscript{7} and O\textsuperscript{1}–P\textsuperscript{1}–C\textsubscript{6} 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 conformation. The P\textsuperscript{1}–O\textsuperscript{1} equatorial bond length is slightly smaller [1.583(5) Å] than the P\textsuperscript{1}–O\textsuperscript{1} and P\textsuperscript{1}–O\textsuperscript{7} axial bond lengths of 1.613(3) and 1.711(5) Å.

The concurrence of the P\textsuperscript{1}–O\textsuperscript{1} and P\textsuperscript{1}–O\textsuperscript{7} axial bond length sum [3.324(5) Å] and O\textsuperscript{1}–...O\textsuperscript{7} distance [3.317(7) Å] can be considered as evidence of the regular trigonal bipyramidal phosphorus configuration. The P\textsuperscript{1}–C\textsubscript{6} bond length is equal to 1.930(7) Å. A five-membered dioxa phospholane cycle occupies the axial-equatorial position in the trigonal bipyramid (O\textsuperscript{1} is axial and O\textsuperscript{5} is equatorial), its configuration is envelope, where four atoms, O\textsuperscript{1}, P\textsuperscript{1}, O\textsuperscript{5} and C\textsubscript{6}, lie in one plane [planar within 0.004(5) Å], and the C\textsuperscript{6} atom deviates from this plane by 0.518(9) Å. The C\textsuperscript{9} and C\textsuperscript{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 C\textsuperscript{10} and C\textsuperscript{11} atoms also deviate from the O\textsuperscript{1}P\textsuperscript{1}O\textsuperscript{2} plane by −0.05(1) and 0.91(1) Å, respectively, and are located in equatorial positions. The O\textsuperscript{2} and C\textsuperscript{6} atoms deviate in opposite sides from the O\textsuperscript{1}P\textsuperscript{1}O\textsuperscript{2} 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 C\textsuperscript{10} and O\textsuperscript{2} deviations are minimal [they deviate by −0.05(1) and −0.213(5) Å, respectively] and we can assume that they lie in the O\textsuperscript{1}P\textsuperscript{1}O\textsuperscript{2} plane.
the above plane by the values of $-1.625(2)$ and $1.700(2) \text{Å}$ [the valence angle of $O^\text{P}\text{-P}^\text{O}^\text{O}$ is equal to $177.5(1)^{\circ}$]. The values of the valence angles $O^\text{P}\text{-P}^\text{O}^\text{O}$, $O^\text{O}\text{-P}^\text{O}^\text{O}$, $O^\text{P}\text{-P}^\text{O}^\text{O}$, $O^\text{O}\text{-P}^\text{O}^\text{O}$, $O^\text{P}\text{-P}^\text{O}^\text{O}$ and $O^\text{O}\text{-P}^\text{O}^\text{O}$ vary within the limits of $86.1(1)$–$92.4(1)^{\circ}$, and the sum of the valence angles of $O^\text{P}\text{-P}^\text{O}^\text{O}$, $O^\text{P}\text{-P}^\text{O}^\text{O}$, $O^\text{P}$ and $O^\text{O}$ 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 $P^\text{O}^\text{P}$, $P^\text{O}^\text{O}$ and $P^\text{O}^\text{O}$ bonds [1.606(2), 1.582(2), and 1.647(2) Å, respectively] are slightly shorter than the axial $P^\text{O}^\text{P}$ and $P^\text{O}$–$O$ bonds [1.625(2) and 1.700(2) Å, respectively]. The fact of practical coincidence of the $P^\text{O}$–$O$ and $P^\text{O}$–$O$ axial bond values sum [3.325(5) Å] and $O^\text{O}$–..–$O^\text{O}$ distance [3.323(7) Å] is in favor of the regular trigonal bipyramidal configuration. The five-membered tetramethylidioxaphospholane cycle occupies the axial-equatorial position in the trigonal bipyramid ($O^\text{P}$ atom is axial and $O^\text{O}$ atom is equatorial). Its conformation is a distorted envelope, where four $O^\text{P}$, $P^\text{O}$, $O^\text{O}$ and $C^\text{C}$ atoms lie in one plane [planar within $0.0482(7)$ Å], and the $C^\text{R}$ atom deviates from the above plane by 0.422(4) Å. The $C^\text{A}$ and $C^\text{A}$ 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 $C^\text{A}$ and $C^\text{A}$ atoms also deviate by the different values of $0.758(5)$ and $-0.178(6)$ Å (they occupy equatorial positions in the cycle). The $O^\text{O}$ and $O^\text{O}$ atoms deviate to opposite sides from the $O^\text{P}$–$O^\text{O}$–$C^\text{C}$ 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 $O^\text{O}$ atom deviation is minimal [$-0.213(5)$ Å]; thus, it can be concluded that this atom lies in the $O^\text{P}$–$O^\text{O}$–$C^\text{C}$ plane. Moreover, it should be noticed that the $O^\text{P}$–$O^\text{O}$–$C^\text{C}$ fragment is turned to be a part of the more extended planar moiety of $C^\text{O}$–$P^\text{O}$–$O^\text{O}$–$O^\text{O}$–$C^\text{C}$ in the molecule [planar within $0.054(4)$ Å]. The plane of the phenyl substituent position 4 ($C^\text{A}$–$C^\text{A}$–$C^\text{A}$–$C^\text{A}$) 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 $O^\text{P}$–$O^\text{O}$–$C^\text{C}$–$O^\text{O}$ cycle of the rigid bicycloheptane system of molecule 14 is an envelope [it contains a planar four-membered $P^\text{O}$–$O^\text{O}$–$C^\text{C}$ fragment within $0.033(2)$ Å, and the $O^\text{O}$ atom deviates from it by $0.806(2)$ Å]. The $O^\text{O}$, $O^\text{O}$, $O^\text{O}$ and $C^\text{A}$ and $C^\text{A}$ 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 $C^\text{A}$ and $C^\text{A}$ 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 $O^\text{P}$–$O^\text{O}$–$C^\text{C}$–$O^\text{O}$ cycle of the rigid bicycloheptane system of molecule 14 is a slightly distorted envelope [four-membered $O^\text{P}$–$O^\text{O}$–$C^\text{C}$ fragment is planar within $0.044(3)$ Å, and the $O^\text{O}$ atom deviates from the above fragment by $-0.851(2)$ Å]. The $O^\text{O}$, $O^\text{O}$, $O^\text{O}$, $C^\text{A}$, $C^\text{A}$ and $C^\text{A}$ 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...
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–O-isomer 14. Thus, the driving force of the PCO/POC-rearrangements 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 (C1) 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 (C1) 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 C1 and C3 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/POC-rearrangement.

Hydrolysis of P–C-isomer 13 leads to the formation of dioxa phospholane 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. The structure of dioxa phospholane 15 was established based on the comparison of its spectral parameters with that described in the literature and XRD.

The geometry of the molecule in a crystal (solvate with water) is presented in Fig. 4. The five-membered cycle of molecule 15 has an envelope conformation, accordingly with a planar O1P2O–C8 fragment within 0.115(4) Å, and the C6 atom deviates from the abovementioned plane by −0.492(8) Å. The O5, C3 and C12 atoms are located in axial positions (they deviate from the O1P1O2C8 plane by 1.574(5), −1.990(8) and 1.552(8) Å, respectively). The O4, C10 and C11 atoms are located in equatorial positions and deviate from the O1P1O2C8 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 O15 oxygen and water molecule protons [O15–H15–O4-interaction, the parameters are O15–H15 0.72(9) Å, H15–O4 2.0(1) Å, O15⋯O4 2.75(1) Å, O15–H15⋯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 O15 [O2–H2⋯O15, interaction, the parameters are O2–H2 0.86(7) Å, H2⋯O15 1.61(7) Å, O2⋯O15 2.46(1) Å, O2–H2⋯O15 168(9)°, and symmetry operation 1 + x, y, z]. Using the classical hydrogen interactions, the molecules in the crystal 15 form ribbons along the 0a crystallographic axis (see Fig. 5).

Mild stepwise hydrolysis of P–O-isomer 14 leads to the initial formation of dioxa phospholane 16. The 31P NMR spectrum of this compound contains a doublet (δp 11.0 ppm, JFCCH 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. 4 Geometry of molecule 15 in a crystal (solvate with water). Selected bond lengths (Å) and bond and torsion angles (°): P1–O4 1.568(6), P1–O2 1.533(7), P1–O3 1.572(6), P1–O5 1.477(6), O1–P1–O2 98.6(2), O1–P1–O2 108.5(3), O2–P1–O4 113.5(3), O2–C8–C9 36.9(6), C9–C7–C8–C11 33.6(8) and C10–C7–C8–C12 34.5(8).

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 phosphorane 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 O1P1O3C7 fragment within 0.080(6) Å, and the C4 atom deviates from this plane by 0.510(9) Å (see Fig. 7). The O3, C10 and C12 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 O1P1O3C8 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 C7–C8 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)°, respectively). The envelope conformation is probably realized in a solution for the investigated compound also, which is confirmed by the non-equivalence of these four methyl groups in NMR 1H and 13C spectra, and also by the different spin–spin coupling constants JPCC, which depend on the P–C–C–C torsion angle values. The same situation is realized for the conformation along the C7–C8 bond (the torsion angles of O6C7C8C9 and C10C9C11C16 are 46.2(9) and −45.2(9)°, 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 C7–C8 bond (the torsion angle of C7C8C9C13 is −166.7(7)°). The structure is realized in the crystal [the parameters of the interaction are O6–H6 0.66(6) Å, H6–O4 2.14(6) Å, O6⋯O4 2.76(1) Å, ∠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 O6–H7⋯F1 and O7–H7⋯O5 classical hydrogen bonds [the parameters are O5–H7 0.87(8) Å, H7⋯F1 2.34(9) Å, O7⋯F1 2.860(9) Å, ∠O7–H7⋯F1 119.8(8)°; and H7⋯O5 2.20(7) Å, O7⋯O5 2.722(8) Å, ∠O7–H7⋯O5 118(6)°, respectively, see Fig. 8].

Prolonged hydrolysis of phosphorane 16 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-3-trifluoromethyl-4,4,4-trifluoro-1,2-diphenylbutylphosphate 17 and pinacol. It should be noted that phosphate 17 (δp 17.4 ppm (CD3CN), δp 17.6 ppm (CDCl3/DMSO-d6, 3 : 1)) exists in equilibrium with the cyclic form 19 (δp 17.4 ppm (CD3CN), δp 17.6 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 °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, C4–C4–enantiomer is shown). Selected bond lengths (Å) and bond and torsion angles (°): P1–O1 1.582(6), P1–O2 1.581(6), P1–O3 1.583(7), P1–O4 1.460(6), O3–C1 1.478(9), O1–P1–O3 101.2(3), O1–P1–O2 99.6(3), O1–P1–O4 118.9(4), O2–P1–O3 109.6(3), O2–P1–O4 112.7(3), O3–P1–O4 113.4(4), P1–O2–C3–C5 163.2(5), O7–C4–C5–O6 165.2(6) and O2–C5–C4–O7 46.1(8).

Fig. 7 Conformation of 1,3,2-dioxaphospholane cycle along the C7–C8 bond in 16 (acyclic substituent is omitted for clarity).
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 $C^3S$-$C^6R$/$C^6S$-$C^3R$. The conformations of the monophosphate 17 and pinacol molecule along the $C^1$-$C^3$, $C^3$-$C^4$ and $C^6$-$C^{68}$ bonds are shown in Fig. 10. All of them are closely related to the almost regular staggered species. The phenol substituents are located in the gauche-conformation along the $C^1$-$C^3$ bond (the torsion angle of $C^{13}$-$C^3$-$C^4$-$C^{19}$ is $-50.1(6)^\circ$).

The trifluoromethyl groups have different orientations relative to the phenyl ring at the $C^3$ atom (see Fig. 10) and therefore fluorine atoms exhibit non-equivalence in the $^{19}$F 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 axis crystallographic plane, and thus, a 2D supramolecular structure is realized in the crystal [the parameters of the interactions are O--H---O(4) interaction: O--H 0.86(6) Å, H---O 1.76(6) Å, O---O 2.547(6) Å, O---H---O 152(9)°; and symmetry operation $x, 1/2 - y, 1/2 + z$; O--H---O---O interaction: O--O 0.98(7) Å, H---O 1.68(7) Å, O---O 2.639(6) Å, O---H---O 165(5)°, and symmetry operation $1 - x, 1 - y, 1 - z$; O--H---O---O interaction: O--O 0.99(9) Å, H---O 1.85(7) Å, O---O 2.802(6) Å, O---H---O 159(9)°, 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 O--H---F classical hydrogen bond [the parameters are O--H 0.99(9) Å, H---F 2.31(9) Å, O---F 2.757(6) Å, and O--H--F 106(7)°, see ES1].

**Experimental**

1-(2,3-Butylenedioxy)-6,6-bis(trifluoromethyl)-3,4-diphenyl-1,2,5,7-phosphatrioxacyclobutylen[2.2.1.4]heptane 13

Hexafluoroacetone (4.81 g, 30 mmol) was condensed into a $\text{CCl}_3/\text{CH}_2\text{Cl}_2$ (1 : 1) solution (40 mL) of dioxaphosphole 12 (10.4 g, 30 mmol) at $-20^\circ$C. The reaction mixture was warmed up to $20^\circ$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 $^\circ$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 ($-18^\circ$C). Clear white crystals of compound 13 were filtered off. Yield 3.62 g (24%), mp 123-125 $^\circ$C.

Anal. calcd for $\text{C}_{23}\text{H}_{23}\text{F}_{6}\text{O}_{5}\text{P}$ (524.12): C, 52.68; H, 4.42; P, 8.42. Found: C, 52.73; H, 4.48; P, 8.61. $\text{IR (KBr)} (\text{cm}^{-1}):$ 3048, 2978, 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. $\text{1H NMR (400 MHz, CDCl}_3)\delta$ (ppm): 7.30 (m, 2H), 7.18 (m, 5H), 7.10 (m, 3H), 5.46 (d, 1H), $J_{\text{FOCH}} = 17.0$ Hz, $H^\alpha$, 1.49 (br. s, 12H, $\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl$_3)$, [hereinafter a view of signal $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is in parentheses] $\Delta\delta$ (ppm): 135.74 (m, d), $3J_{\text{HC}} = 7.7$ Hz, $2J_{\text{HC}} = 5.2$ Hz, $J_{\text{PO(Cl)}} = 0.7$ Hz, $J_{\text{HC}} = 133.36$ (dt, d), $J_{\text{FOCC}} = 12.6$ Hz, $J_{\text{FOCC}} = 7.5$ Hz, $C^{19}$, 129.18 (dt, d), $J_{\text{HC}} = 160.7$ Hz, $J_{\text{HC}} = 2.3$ Hz, $C^{19}$, 128.61 (ddm, d), $J_{\text{HC}} = 161.0$ Hz, $J_{\text{HC}} = 7.2$ Hz, $J_{\text{HC}} = 128.09$ (br. dd, s), $J_{\text{HC}} = 160.3$ Hz, $J_{\text{HC}} = 7.4$ Hz, $C^{15,19}$, 127.90 (dd, d), $J_{\text{HC}} = 161.0$ Hz, $J_{\text{HC}} = 7.0$ Hz, $C^{21,13}$, 127.21 (br. ddd, s), $J_{\text{HC}} = 159.6$ Hz, $J_{\text{HC}} = 6.2$ Hz, $J_{\text{HC}} = 6.2$ Hz, $J_{\text{HC}} = 6.2$ Hz, $C^{14,18}$, 125.82 (ddd, d), $J_{\text{HC}} = 161.1$ Hz, $J_{\text{HC}} = 7.4$ Hz, $J_{\text{HC}} = 6.2$ Hz, $C^{23,24}$, 122.60 (qd, qd), $J_{\text{HC}} = 285.8$ Hz, $J_{\text{FOCC}} = 1.1$ Hz, $C^{26}$, 121.71 (br. qd, qd), $J_{\text{HC}} = 289.8$ Hz, $J_{\text{FOCC}} = 5.7$ Hz, $C^{23}$). 99.76 (ddm, d), $J_{\text{FOCC}} = 23.9$ Hz, $J_{\text{HC}} = 4.2$ Hz, $J_{\text{HC}} = 4.2$ Hz, $C^{1}$, 87.68 (ddm, d), $J_{\text{HC}} = 156.3$ Hz, $J_{\text{FOCC}} = 2.9$ Hz, $J_{\text{HC}} = 4.4$ Hz, $C^{1}$, 82.93 (m, d), $J_{\text{FOCC}} = 2.2$ Hz, $J_{\text{HC}} = 4.2$ Hz, $J_{\text{HC}} = 4.2$ Hz, $C_{\text{ax}}$, 79.17 (m, d), $J_{\text{FOCC}} = 2.9$ Hz, $J_{\text{HC}} = 4.4$ Hz, $C_{\text{ax}}$, 77.78 (d. sept, d. sept), $J_{\text{HC}} = 154.8$ Hz,
A mixture of compound 13 (6.00 g, 11.45 mmol) and CDCl3 (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. calc. 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) (νmax cm−1): 3067, 3036, 2984, 2938, 1500, 1460, 1452, 1396, 1378, 1288, 1241, 1164, 1013, 1042, 984, 928, 899, 897, 893, 833, 805, 783, 754, 738, 714, 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, JH1C = 19.2 Hz, H2), 1.52 (s, 3H, CH3), 1.51 (s, 3H, CH3), 1.43 (s, 3H, CH3), 1.38 (s, 3H, CH3). 31P NMR (161.0 MHz, CDCl3)/δ (ppm): −7.0 Hz, C15,17), 128.86 (dd (s), JH2C = 7.3 Hz, H3C13). To a suspension of compound 14 (3.54 g, 6.75 mmol) in 10 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, DMSO-d6), δ: 8.72 (br, s, 1H, OH), 1.41 (br, s, 12H, H214), 31P NMR (161.9 MHz, DMSO-d6), δp 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. The filtrate was evaporated in vacuo (14 Torr) to give a white precipitate of benzoin, mp 132−134 °C. 1H NMR (600 MHz, acetone-d6), δ: 8.03 (m, 2H, X′-part of AA′XX′-subsystem, JAX = JAX′ = 7.5 Hz, H20,24, 7.56 (tt, 1H, JAM = JAM′ = 7.5 Hz), JXM = JXM′ = 1.5 Hz, M-part of AA′MXX′-system, H22, 7.45 (br. dd, 2H, A′-part of AA′XX′-system, JAM = JAM′ = 7.5 Hz, H15,17), 7.32 (br dd, 2H, AA′-part of AMMXX′-system, JXM = JXM′ = 7.5 Hz, H14,15), 6.22, 5.5 Hz). ESI-MS (m/z): 300.01 (br. dt (s), JHC = 3.5 Hz, 1H, H14,15). 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 3 mL of diethyl ester was added dropwise with constant stirring. The resulting white crystalline precipitate of compound 15 (hydrate...
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, DMSO-d6) δ (ppm): −66.49 (br. q, J_FCCCF = 10.9 Hz), −68.10 (br. q, J_FCCCF = 10.9 Hz), 31P/31P-{1H} NMR (161.9 MHz, DMSO-d6) δ (ppm): 10.7 (d, J_FCCCF = 7.8 Hz). MALDI-MS (m/z): 565.03 (M + Na), 580.93 (M + K).

Found: C, 47.74; H, 5.00; P, 5.31. IR (nujol) (νmax, cm⁻¹): 3524, 3499, 3282, 3068, 2349, 1736, 1681, 1601, 1497, 1452, 1377, 1277, 1213, 1154, 1114, 1074, 1022, 1001, 967, 935, 761, 727, 711, 699, 624, 612, 541, 523, 494, 463. 1H NMR (400 MHz, CDCl3)/δ (ppm): 7.46 (br. d, 2H, H20,24), 7.21 (d, J_HHCH = 7.1 Hz, 2H, H14,18), 7.10 (m, 3H, H9,20,21), 7.04 (m, 3H, H15,16,17), 6.09 (d, J_FPOCH = 4.9 Hz, 1H, H1), 1.16 (s, 12H, Me, pinacol), 1.13C/13C-{1H} NMR (100.6 MHz, CD2Cl2)/δ (ppm): 137.98 (br. td (br. s), J_FCCCF = 5.5, C19), 137.07 (br. td (br. s), J_FCCCF = 7.3 Hz, C18), 131.10 (br. d (s), J_FCCCF = 156.6 Hz, C14,15), ~127.9 (v. br. d (v. br. s), J_FCCCF = 20.3), 128.71 (br. dt (s), J_HHCH = 161.4 Hz, C14,15), 126.64 (br. dt (s), J_HHCH = 161.7 Hz, C22), 125.10 (br. dd (s), J_HHCH = 158.5 Hz, J_FCCCF = 7.3 Hz, C15,17), 127.85 and 126.74 (two v. br. d (two v. br. s), J_FCCCF = 20.29 and C12,13), 123.35 (q (q), J_FCCCF = 289.4 Hz, CF3), 124.18 (q (q), J_FCCCF = 290.9 Hz, CF3), 90.34 (m (s), pinacol), 83.79 (sept (sept), J_FCCCF = 25.7 Hz, C5), 83.12 (d (d), J_HHCH = 151.5 Hz, J_FCCCF = 2.6 Hz, C5, 81.87 (m (d), J_FCCCF = 8.1 Hz, C4), 25.16 (q (q), J_HHCH = 125.4, CH3, pinacol). 31P NMR (376.4 MHz, CDCl3)/Δδ (3 : 1)/δ (ppm): −67.05 (q, J_FCCCF = 11.2 Hz), −67.82 (q, J_FCCCF = 10.2 Hz), 31P/31P-{1H}NMR (161.9 MHz, CD2Cl2)/δ (ppm): −1.4 (br. s (s)).

Crystal structure determination

Crystal structures were determined by X-ray diffraction of suitable monocryrstals. Crystal data were collected at 296 K using graphite monochromatic MoKα (0.7073 Å) radiation and w-scans. Data collection images were indexed, integrated, and scaled using the APEX2 data reduction package. Multi-scan empirical absorption corrections were applied to all data sets, where appropriate, using the SADABS program. The structures were solved and refined using the SHELX97 program. All crystal structure pictures were created using Mercury CSD 2.4.

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 C23H23F6O5P (578.44): C, 47.76; H, 5.05; P, 5.35.
0.0499, wR2 = 0.1437 for 1316 reflections with I > 2σ(I); R1 = 0.0907, wR2 = 0.1841 for all data.

Crystal data for 16

C123H25F6O6P, M = 542.40, triclinic, a = 10.788(13), b = 10.889(13), c = 12.329(15) Å, α = 70.63(2), β = 71.74(2), γ = 67.88(2)°, V = 1236(3) Å3, T = 296 K, space group P1 (no. 2), Z = 2, 4706 reflections measured, which were used in all calculations. Final indices R1 = 0.0880, wR2 = 0.2734 for 2147 reflections with I > 2σ(I); R1 = 0.1946, wR2 = 0.3522 for all data.

Crystal data for 18

C17H15F6O6P 0.5C6H14O2, M = 519.34, monoclinic, a = 18.721(8), b = 13.944(6), c = 8.706(4) Å, β = 95.489(8)°, V = 2262(2) Å3, T = 296 K, space group P21/c (no. 14), Z = 4, 41470 reflections measured, 4448 unique (Rint = 0.152), which were used in all calculations. Final indices R1 = 0.0773, wR2 = 0.1632 for 1683 reflections with I > 2σ(I); R1 = 0.2229, wR2 = 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-dioxaphospholine 12 with hexafluoroacetone results in the simultaneous formation of regioisomeric cage (P-C-P-O)-phosphoranes 13 and 14 in the ratio of 1:1. 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-trifluorobutyl-oxo)-4,4,5,5-tetramethyl-2-oxo-1,3,2-dioxaphospholane with the same configurations for the C3 and C4 atoms, and further hydrolysis of this compound yields 2,3-dihydroxy-3-trifluoromethyl-4,4,4-trifluoro-1,2-diphenyl butylyphosphate 17 and pinacol.

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