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Reactions of 2-Phenyl-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,2-benzodioxaphosphepin-5-one with Phenanthrenequinone and Dibenzoyl

V. F. Mironov[a, b], L. M. Burnaeva[b], Yu. Yu. Borisova[b], A. T. Gubaidullin[a], I. A. Litvinov[a], G. A. Ivkova[b], and I. V. Konovalova[b]

[a] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia*
e-mail: mironov@iopc.ru

[b] *Privolzhsk (Kazan) Federal University, Kazan, Tatarstan, Russia*

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Abstract—Reactions of 2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,2-benzodioxaphosphepin-5-one with 9,10-phenanthrenequinone and dibenzoyl gave hydrolytically unstable spirophosphoranes with five- and seven-membered rings, 2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydrospiro[[1,3,2]benzodioxaphosphepine-2,2′-phenanthro[9,10-*d*][1,3,2]dioxaphosphol]-5-one and 2,4′,5′-triphenyl-4,4-bis(trifluoromethyl)-4,5-dihydrospiro[[1,3,2]benzodioxaphosphepine-2,2′-[1,3,2]dioxaphosphol]-5-one. The structure of the first of these was proved by X-ray analysis.

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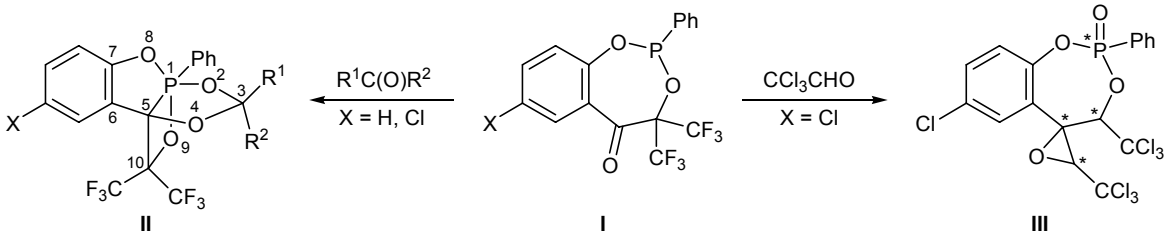
Tervalent phosphorus derivatives are key precursors of various organophosphorus compounds with different coordination numbers of the phosphorus atom [1–4]. This is related to accessibility of lone electron pair on the phosphorus atom and thermodynamic favorability for the formation of phosphoryl compounds. Cyclic phosphorylated derivatives of salicylic acid having a fairly reactive carbonyl group in the β-position with respect to the phosphorus atom occupy a specific place among P(III) compounds. They are capable of being involved in cascade reactions with activated carbonyl compounds, Schiff bases, and ylidene derivatives of dicarbonyl compounds. In these reactions, the carbonyl group can participate in one or another step of the cascade process, leading to the formation of 1,3,2-dioxa(oxaza)- and 1,4,2-dioxa(oxaza)phosphepines, 1,2-oxaphospholanes, and other difficultly accessible compounds [5–12].

We recently showed that cyclic phosphorus(III) derivatives having an activated carbonyl group in the γ-position with respect to the phosphorus atom, e.g., 2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,2-benzodioxaphosphepin-5-one (**I**), also undergo cascade transformations by the action of trichloroacetaldehyde and hexafluoroacetone. As a result, cage-like propeller phosphorane with a phosphorus–carbon bond (structure **II**) [13, 14] or spiran structure **III** is formed; in the latter structure, the γ-carbonyl carbon atom becomes a spiro atom [15] (Scheme 1).

Scheme 1.

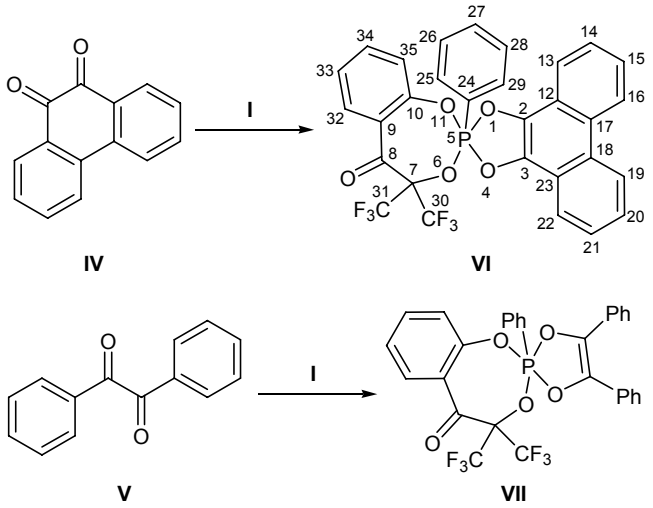


$R^1 = R^2 = CF_3$; $R^1 = CCl_3$, $R^2 = H$.

While developing the above approach, in the present work we performed reactions of benzodioxaphosphepine **I** with α-dicarbonyl compounds, 9,10-phenanthrenequinone (**IV**) and dibenzoyl (**V**, benzil). It is known that α-diketones react with common trialkyl phosphites to produce 1,3,2-dioxaphospholes [16]; in some cases, these compounds are unstable and are readily converted into more stable four-coordinate phosphorus compounds, the dioxaphosphole ring being conserved [17] or opened [16]. The stability of λ^5-dioxaphosphole structure increases in going from acyclic phosphites to five-membered cyclic P(III) derivatives [18]. Dialkoxy-λ^3-phosphanyl isocyanates having a carbonyl group in the β-position with respect to the phosphorus atom reacted with diacetyl and dibenzoyl either at both carbonyl groups to afford cycloaddition products, 1,3,2-dioxaphospholes, or at the isocyanate carbonyl group with formation of oxazaphospholanes having P–C and P–O bonds in the ring [19]. Dibenzoyl reacted with "salicyl" phosphites along two pathways, yielding 1,3,2-dioxaphosphepine and spirocyclic pentaalkoxyphosphorane, and the latter underwent thermal decomposition to phosphole derivative via elimination of salicylic fragment [20].

The reactions of compound **I** with 9,10-phenanthrenequinone (**IV**) and dibenzoyl (**V**) occurred under mild conditions (2 months at 20–25°C; Scheme 2).

Scheme 2.



According to the $^{31}P–\{^1H\}$ NMR data, the products were spirophosphorane compounds, 2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydrospiro[[1,3,2]benzodioxaphosphepine-2,2′-phenanthro[9,10-*d*][1,3,2]dioxaphosphol]-5-one (**VII**, δ_P –31.9 ppm) and 2,4′,5′-triphenyl-4,4-bis(trifluoromethyl)-4,5-dihydrospiro[[1,3,2]benzodioxaphosphepine-2,2′-[1,3,2]dioxaphosphol]-5-one (**VII**, δ_P –37.6 ppm).

The IR spectrum of phosphorane **VI** contained an absorption band at 1699 cm^{-1} typical of stretching vibrations of ketone carbonyl group, and two quartets belonging to two nonequivalent trifluoromethyl groups were present in its ^{19}F NMR spectrum at δ_F –70.78 and –72.05 ppm ($^4J_{FF}$ = 9.2 Hz). Analogous pattern was observed in the ^{19}F NMR spectrum of **VII** (δ_F –70.81, –72.0 ppm, $^4J_{FF}$ = 9.1 Hz). The carbonyl carbon atom resonated in the ^{13}C NMR spectrum of **VI** at δ_C 188.88 ppm. Thus the carbonyl group in cyclic phosphonite **I** does not participate in the reactions with quinone **IV** and diketone **V**, presumably due to steric hindrances in carbonyl compounds **IV** and **V**, which prevent formation of phosphorane structure analogous to that formed in the reaction with trichloroacetaldehyde [14].

Crystalline phosphorane **VI** was isolated by keeping the reaction mixture at low temperature in an inert atmosphere. Its structure was proved by X-ray analysis (Fig. 1); the principal geometric parameters of molecule **VI** are given in table. The phosphorus atom has a trigonal bipyramid configuration with axial–equatorial orientation of the dioxaphosphole and dioxaphosphepine rings: the O^1 and O^{11} atoms occupy axial positions, and the O^4 and O^6 atoms and the phenyl group are equatorial. The seven-membered heteroring adopts a distorted *boat* conformation with the planar [within 0.020(4) Å] $C^8C^9C^{10}O^{11}$ four-atom fragment; the P^1, O^6, and C^7 atoms deviate from that plane toward one side by different distances, which defines *boat* conformation. The five-membered $P^5O^1C^2C^3O^4$ ring is planar, and it lies in the same plane with the phenanthrene system. On the whole, structural parameters of molecule **VI** are similar to those reported previously for spirophosphoranes consisting of one five-membered ring and one seven-membered ring [21].

Phosphorane **VI** displays a variety of intermolecular interactions in the crystalline structure. π-Electron interactions between the aromatic phenanthrene fragments related to each other through a symmetry center ($2 - x$, $1 - y$, $1 - z$) give rise to π-dimers, the distance between the centroids of the phenanthrene rings being 3.57 Å (the shortest distance between their planes is 3.42 Å, and the dihedral angle is 0°). The same molecules are also linked through pair C–H···F interactions with the following parameters: $H^{16}\cdots F^{302}$ 2.48 Å, $\angle C^{16}H^{16}F^{302}$ 163° (Fig. 2). The other interactions (C–H···O, C–F···π, and C–H···π) lead to the forma-

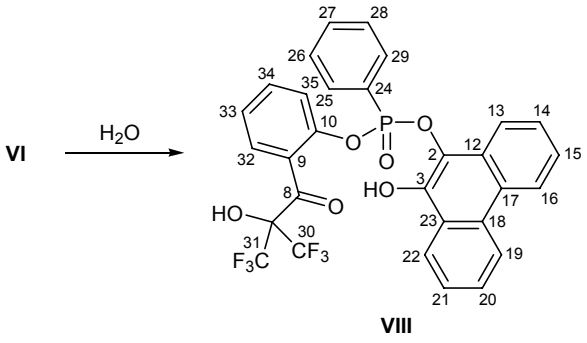
Selected bond lengths (*d*, Å) and bond (ω, deg) and dihedral angles (φ, deg) in the molecule of 2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydrospiro[[1,3,2]benzodioxaphosphepine-2,2′-phenanthro[9,10-*d*][1,3,2]dioxaphosphol]-5-one (**VI**)

Bond	*d*, Å	Angle	ω, deg	Angle	φ, deg
P^5–O^1	1.626(3)	$O^1P^5O^6$	125.0(2)	$O^{11}P^5O^6C^7$	21.1(3)
P^5–O^6	1.633(3)	$O^1P^5O^{11}$	86.8(1)	$O^6P^5O^{11}C^{10}$	72.3(3)
P^5–O^{11}	1.669(3)	$O^6P^5O^{11}$	92.6(1)	$C^{24}P^5O^{11}C^{10}$	–171.8(3)
P^5–O^4	1.715(3)	$O^1P^5O^4$	89.8(1)	$P^5O^6C^7C^8$	–66.3(5)
P^5–C^{24}	1.802(4)	$O^6P^5O^4$	84.1(1)	$O^6C^7C^8O^8$	–162.4(4)
O^1–C^2	1.391(4)	$O^{11}P^5O^4$	172.7(2)	$O^8C^8C^9C^{10}$	–147.7(5)
O^4–C^3	1.358(5)	$O^1P^5C^{24}$	119.2(2)	$O^8C^8C^9C^{32}$	25.5(7)
O^6–C^7	1.425(5)	$O^6P^5C^{24}$	115.8(2)	$C^7C^8C^9C^{32}$	–152.9(4)
O^8–C^8	1.201(5)	$C^2O^1P^5$	114.7(2)	$P^5O^{11}C^{10}C^9$	–81.4(4)
O^{11}–C^{10}	1.381(4)	$C^3O^4P^5$	112.4(2)		
C^2–C^3	1.352(5)	$C^7O^6P^5$	133.4(2)		
C^7–C^8	1.565(5)	$C^{10}O^{11}P^5$	120.8(2)		
C^8–C^9	1.477(6)	$O^6C^7C^8$	116.5(3)		
C^9–C^{10}	1.388(6)	$O^8C^8C^9$	122.5(4)		
C^7–C^{31}	1.543(6)	$O^8C^8C^7$	115.6(4)		

tion of a three-dimensional network in crystal; the calculated packing index is fairly high (70.3%).

Mild hydrolysis of phosphorane **VI** ($CDCl_3$, atmospheric moisture) involved opening of both dioxaphosphepine and dioxaphosphole rings and afforded 9-hydroxyphenanthren-10-yl 2-(3,3,3-trifluoro-2-hydroxy-1-oxo-2-trifluoromethylpropyl)phenyl phenylphosphonate (**VIII**, δ_P 21.2 ppm; Scheme 3).

Scheme 3.



Compound **VIII** showed in the ^{19}F NMR spectrum a singlet at δ_F –72.86 ppm due to two equivalent trifluoromethyl groups. The phosphorus nucleus in **VIII** resonated in the ^{31}P NMR spectrum as a broadened triplet of triplets at δ_P 21.3 ppm ($^3J_{PH}$ = 14.5, $^4J_{PH}$ = 4.5 Hz). The structure of **VIII** was confirmed by the ^{13}C, ^{13}C–{^1H}, APT (^{13}C, ^1H), and ^1H–^1H COSY spectra. Nonequivalence of carbon nuclei and protons in the phenanthrene fragment of **VIII** (as compared to cyclic structure **VI**), as well as the absence of coupling between the phosphorus atom and C^7 (δ_C 82.59 ppm, septet, $^2J_{CF}$ = 28.7 Hz), also indicated acyclic structure of compound **VIII**. Hydrolytic stability of four-coordinate phosphorus derivatives having a hydroxyphen-

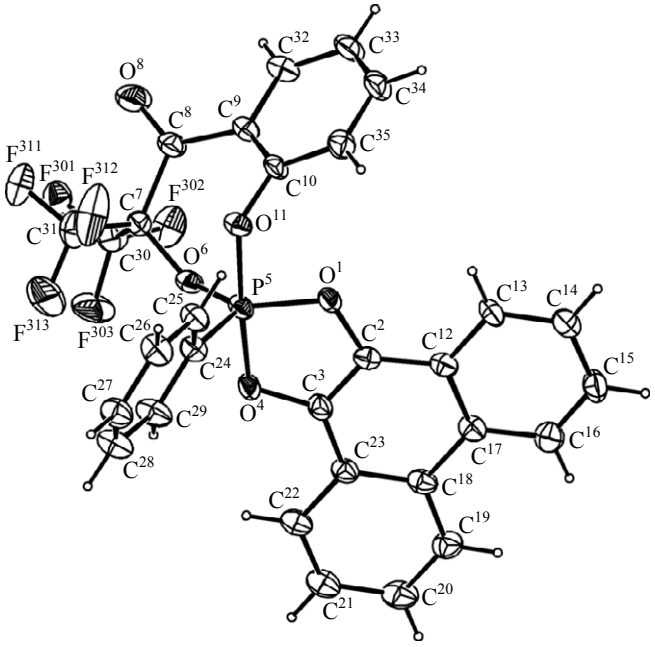


Fig. 1. Structure of the molecule of 2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydrospiro[[1,3,2]benzodioxaphosphepine-2,2′-phenanthro[9,10-*d*][1,3,2]dioxaphosphol]-5-one (**VI**) according to the X-ray diffraction data.

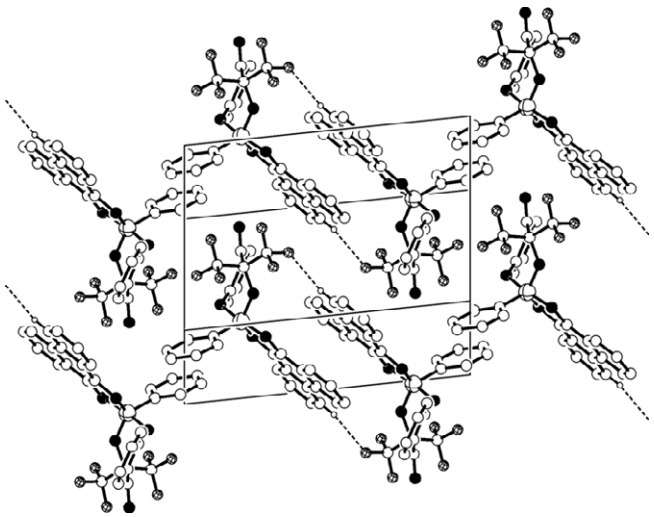


Fig. 2. A fragment of crystal packing of phosphorane **VI** (view along the 0*y* axis). Only hydrogen atoms involved in C–H···F interactions (dashed lines) are shown.

anthrene fragment was noted previously [21–24]; it was attributed to formation of intramolecular hydrogen bond between the hydroxy and phosphoryl groups.

Thus the reaction of 2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,2-benzodioxaphosphepin-5-one with 9,10-phenanthrenequinone and benzil does not involve the carbonyl group in the former and yields hydrolytically unstable spirophosphoranes with five- and seven-membered rings.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer from samples dispersed in mineral oil (between KBr plates) or pelleted with KBr. The NMR spectra were measured on Varian Unity-300 (300 MHz for ^{1}H, 121.42 MHz for ^{31}P, and 282.4 MHz for ^{19}F), Bruker Avance-600 (600 MHz for ^{1}H, 150.9 MHz for ^{13}C, and 243.0 MHz for ^{31}P), and Bruker MSL-400 instruments [100.6 MHz; ^{13}C, ^{13}C–{^{1}H})]. The ^{1}H and ^{13}C chemical shifts were determined relative to the corresponding solvent signals ($CDCl_3$). The ^{31}P chemical shifts were measured relative to H_3PO_4 as external reference, and the ^{19}F chemical shifts were determined relative to hexafluorobenzene as internal reference and were then recalculated to $CFCl_3$.

X-Ray analysis of compound VI. The X-ray diffraction data were acquired on an Enraf–Nonius CAD-4 diffractometer at 20°C (λCuK_α, $\theta_{max} < 74.35°$). Triclinic crystals with the following unit cell parameters (20°C): a = 9.191(2), b = 10.028(3), c = 14.280(4) Å; α = 88.51(2), β = 84.16(2), γ = 71.61(2)°; V = 1242.4(6) Å^3; Z = 2; space group P-1; M 1204.8; $C_{30}H_{17}F_6O_5P$; d_{calc} = 1.61 g/cm^3; $F(000)$ = 612. Total of 5376 reflection intensities were measured, 3141 of which were characterized by $I > 2\sigma$. No reduction in intensity of three control reflections was observed during the data acquisition process. Absorption by the crystal was taken into account empirically (μ_{Cu} = 17.86 cm^{-1}). The data were acquired and processed using an Alpha Station 200 PC (MolEN software) [25]. The structure was solved by the direct method using SIR program [26] and was refined first in isotropic and then in anisotropic approximation using SHELX97 software [27]. Hydrogen atoms were placed into calculated positions which were refined according to the riding model. All calculations were performed with the aid of WinGX [28]. The final divergence factors were R = 0.062 and wR_2 = 0.153 (for 5076 independent reflections). Intermolecular contacts in crystal, including hydrogen bonds, were analyzed using PLATON program [29].

The coordinates of atoms in structure **VI** and their temperature parameters were deposited to the Cambridge Crystallographic Data Center (*http://www.ccdc.cam.ac.uk;* entry no. CCDC 740323).

2-Phenyl-4,4-bis(trifluoromethyl)-4,5-dihydrospiro[[1,3,2]benzodioxaphosphepine-2,2′-phenanthro[9,10-*d*][1,3,2]dioxaphosphol]-5-one (VI). 9,10-Phenanthrenequinone (**IV**), 1.87 g (0.009 mol), was added at 20°C under dry argon to a mixture 3.54 g (0.009 mol) of dioxaphosphepine **I** and 30 ml of methylene chloride. The mixture was left to stand for 2 months at room temperature (20°C) and then kept for 24 h at 0°C. The crystalline product was filtered off and dried under reduced pressure (12 mm). Yield 89%, mp 140°C. IR spectrum, cm^{-1}: 3378, 3076, 3033, 1969, 1946, 1913, 1884, 1827, 1794, 1699, 1669, 1617, 1604, 1584, 1519, 1479, 1454, 1411, 1377, 1338, 1230, 1164, 1116, 1061, 1031, 979, 959, 942, 876, 844, 822, 771, 750, 719, 686, 668, 655, 626, 609. ^{13}C NMR spectrum ($CDCl_3$, 100.6 MHz), δ_C, ppm (hereinafter, the multiplicity of the corresponding signal in the ^{13}C–{^{1}H} NMR spectrum is given in parentheses; for atom numbering, see Schemes 2 and 3): 84.71 sept.d (sept.d) (C^7, $^{2}J_{CF}$ = 30.0, $^{2}J_{CP}$ = 12.0 Hz), 120.55 d.d (s) (C^{16}, $^{1}J_{CH}$ = 162.2, $^{3}J_{CH}$ = 7.8 Hz), 120.72 q.d (q.d) (C^{30}F$_3$, $^{1}J_{CF}$ = 296.2, $^{3}J_{CP}$ = 4.2 Hz), 120.98 q.d (q.d) (C^{31}F$_3$, $^{1}J_{CF}$ = 289.3, $^{3}J_{CP}$ = 10.2 Hz), 121.71 d.d.d (d) (C^9, $^{3}J_{CP}$ = 11.4, $^{3}J_{CH}$ = 7.8, 7.8 Hz), 123.14 d.d (s) (C^{14}, $^{1}J_{CH}$ = 157.4, $^{3}J_{CH}$ = 7.2 Hz), 123.51 d.d.d (d) (C^{35}, $^{1}J_{CH}$ = 164.6, $^{3}J_{CH}$ = 7.2, $^{3}J_{CP}$ = 6.6 Hz), 125.03 d.d (s) (C^{33}, $^{1}J_{CH}$ = 164.6, $^{3}J_{CH}$ = 9.0 Hz), 125.10 s (d.d)

(C^{13}, $^1J_{CH}$ = 161.0, $^3J_{CH}$ = 8.4 Hz), 126.86 m (br.s) (C^{12}), 127.06 d.d (s) (C^{15}, $^1J_{CH}$ = 161.6, $^3J_{CH}$ = 8.4 Hz), 127.89 m (br.s) (C^{17}), 128.21 d.d.d (d) (C^{26}, $^1J_{CH}$ = 162.2, $^3J_{CP}$ = 19.2, $^3J_{CH}$ = 7.2 Hz), 130.80 d.d (s) (C^{32}, $^1J_{CH}$ = 165.8, $^3J_{CH}$ = 8.4 Hz), 132.47 d.m (d) (C^{27}, $^1J_{CH}$ = 165.2, $^3J_{CH}$ = 7.2, $^4J_{CP}$ = 3.6 Hz), 133.16 d.t (d) (C^{24}, $^1J_{PC}$ = 238.5, $^3J_{CH}$ = 7.8 Hz), 133.62 d.d.d.d (d) (C^{25}, $^1J_{CH}$ = 165.2, $^2J_{CP}$ = 10.8, $^3J_{CH}$ = 7.2, 7.2 Hz), 134.91 m (d) (C^2, C^3, $^2J_{CP}$ = 2.4 Hz), 136.09 d.d (s) (C^{34}, $^1J_{CH}$ = 161.6, $^3J_{CH}$ = 9.0 Hz), 152.52 d.d.d (d) (C^{10}, $^2J_{CP}$ = 12.0, $^3J_{CH}$ = 8.4, 8.4 Hz), 188.88 d (s) (C^8, $^3J_{CH}$ = 3.0 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –72.05 q ($^4J_{FF}$ = 9.2 Hz), –70.78 q ($^4J_{FF}$ = 9.2 Hz). ^{31}P–{^{1}H} NMR spectrum ($CDCl_3$, 121.42 MHz): δ_P –31.9 ppm (s). Found, %: C 59.63; H 2.94. $C_{30}H_{17}F_6O_5P$. Calculated, %: C 59.80; H 2.82.

Spirophosphorane **VI** underwent hydrolysis on exposure to atmospheric moisture under mild conditions (when its solution in $CDCl_3$ was kept at 20°C) to give compound **VIII** which was isolated as fine colorless crystals with mp 137°C. ^{1}H NMR spectrum (acetone-d_6, 600 MHz), δ, ppm: 7.04 d.d.d (1H, 33-H, $^3J_{32,33}$ = 8.3, $^3J_{34,33}$ = 7.2, $^4J_{35,33}$ = 1.2 Hz), 7.09 br.d.d.d (1H, 35-H, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.2, $^4J_{HP}$ = 0.5–0.6 Hz), 7.52 m and 7.56 m (2H, 14-H, 15-H, $^3J_{13,14}$ = 8.1, $^3J_{15,14}$ = 7.1, $^4J_{16,14}$ = 1.2, $^3J_{16,15}$ = 8.2, $^3J_{14,15}$ = 7.1, $^4J_{13,15}$ = 1.4 Hz), 7.54 m (2H, 26-H), 7.62 m (1H, 27-H), 7.64 d.d.d (1H, 34-H, $^3J_{35,34}$ = 8.4, $^3J_{33,34}$ = 7.2, $^4J_{32,34}$ = 1.4–1.5 Hz), 7.68–7.70 m (2H, 20-H, 21-H, *AB* part of *ABMX* spin system), 8.05 br.d.d (1H, 13-H, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.2 Hz), 8.08 br.d.d.m (2H, 25-H, $^3J_{HP}$ = 15.5, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.3 Hz), 8.41 br.d.d (1H, 32-H, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 1.4–1.5 Hz), 8.46 m (1H, 22-H), 8.68 br.d (1H, 16-H, $^3J_{HH}$ = 8.2 Hz), 8.73 m (1H, 19-H). ^{13}C NMR spectrum (acetone-d_6, 150.9 MHz), δ_C, ppm: 82.59 sept (sept) (C^7, $^2J_{CF}$ = 28.7 Hz), 118.52 d.d (s) (C^{19}, $^1J_{CH}$ = 162.9, $^3J_{CH}$ = 7.6 Hz), 119.84 br.d.d (s) (C^9, $^3J_{CH}$ = 7.4, 5.5 Hz), 119.84 d.d (s) (C^{16}, $^1J_{CH}$ = 164.9–65.0, $^3J_{CH}$ = 8.0 Hz), 121.38 d.d (s) (C^{22}, $^1J_{CH}$ = 161.6, $^3J_{CH}$ = 7.4 Hz), 122.13 br.q (br.q) (C^{30}, C^{31}, $^1J_{FC}$ = 289.3 Hz), 122.97 d.d (s) (C^{13}, $^1J_{CH}$ = 157.5–158.0, $^3J_{CH}$ = 7.7 Hz), 122.97 d.d.d (d) (C^{35}, $^1J_{CH}$ = 157.5–158.0 Hz, overlapped by the C^{13} signal), 123.52 d.d.d (s) (C^{20}, $^1J_{CH}$ = 162.2, $^3J_{CH}$ = 5.1, $^2J_{CH}$ = 3.5 Hz), 125.10 d.d (s) (C^{15}, $^1J_{CH}$ = 161.3, $^3J_{CH}$ = 8.3 Hz), 126.94 m (s) (C^{23}), 127.17 d.d (s) (C^{21}, $^1J_{CH}$ = 160.9, $^3J_{CH}$ = 7.4 Hz), 127.26 d.d (s) (C^{14}, $^1J_{CH}$ = 160.8, $^3J_{CH}$ = 8.4 Hz), 127.45 br.d.d (s) (C^{33}, $^1J_{CH}$ = 160.5, $^3J_{CH}$ = 8.0 Hz), 127.75 br.d.t (d) (C^{24}, $^1J_{CP}$ = 189.0, $^3J_{CH}$ = 7.8 Hz), 127.82 m (s) (C^{12}), 128.24 d.d.d (d) (C^2, $^2J_{CP}$ = 8.8, $^3J_{CH}$ = 4.7, $^4J_{CH}$ = 1.5 Hz), 128.38 m (s) (C^{17})129.10 d.d.d (d) (C^{26}, $^1J_{CH}$ = 160.9, $^3J_{CP}$ = 15.5, $^3J_{CH}$ = 8.3 Hz), 129.52 m (s) (C^{18}), 132.17 d.d.d.d (d) (C^{25}, $^1J_{CH}$ = 163.1, $^2J_{CP}$ = 10.5, $^3J_{CH}$ = 7.4, 7.4 Hz), 132.36 br.d.d (s) (C^{32}, $^1J_{CH}$ = 164.4, $^3J_{CH}$ = 8.1 Hz), 133.66 d.t.d.d (br.s) (C^{27}, $^1J_{CH}$ = 162.5, $^4J_{CP}$ = 2.9, $^3J_{CH}$ = 7.6, $^2J_{CH}$ = 1.4 Hz), 137.94 d.d.d (s) (C^{34}, $^1J_{CH}$ = 161.2, $^3J_{CH}$ = 9.2, $^2J_{CH}$ = 1.8 Hz), 140.75 br.d.d (br.d) (C^3, $^2J_{CP}$ = 2.3, $^3J_{CH}$ = 3.5–4.0 Hz), 162.22 m (br.s) (C^{10}, $^2J_{CP}$ = 2.0, $^3J_{CH}$ = 9.8, 7.8, $^2J_{CH}$ = 1.5 Hz), 194.10 br.d (s) (C^8, $^3J_{CH}$ = 3.9 Hz). ^{19}F NMR spectrum (acetone-d_6): δ_F –72.86 ppm, s. ^{31}P NMR spectrum (acetone-d_6, 243.0 MHz): δ_P 21.2 ppm, br.t.t ($^3J_{PH}$ = 15.2, $^4J_{PH}$ = 4.5 Hz). Found, %: C 59.67; H 3.11. $C_{30}H_{17}F_6O_5P$. Calculated, %: C 59.80; H 2.82.

2,4′,5′-Triphenyl-4,4-bis(trifluoromethyl)-4,5-dihydrospiro[[1,3,2]benzodioxaphosphepine-2,2′-[1,3,2]dioxaphosphol]-5-one (VII). Dibenzoyl (**V**), 2.53 g (0.012 mol), was added at 20°C under argon to a solution of 4.74 g (0.012 mol) of compound **I** in 30 ml of methylene chloride. The mixture was kept for 2 months at 20°C and then for 2 days at 0°C, and the precipitate was filtered off and dried under reduced pressure (12 mm). Yield 81%, mp 78–82°C. ^{31}P–{^{1}H} NMR spectrum ($CDCl_3$, 121.42 MHz): δ_P –36.9 ppm. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –70.6 q ($^4J_{FF}$ = 9.1 Hz), –72.3 q ($^4J_{FF}$ = 10.7 Hz). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz): δ 6.92–8.55 ppm, m. Found, %: C 60.08; H 3.37. $C_{30}H_{19}F_6O_5P$. Calculated, %: C 59.60; H 3.15.

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