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2-Polyfluoroalkoxy-1,3,2-dioxaphosphorinanes

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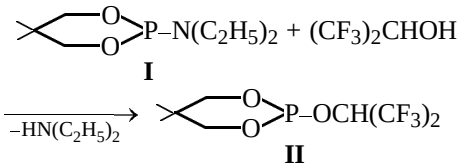
Abstract — 2-Polyfluoroalkoxy-1,3,2-dioxaphosphorinanes and related phosphocyclic compounds were prepared by alcoholysis of 2-amino-1,3,2-dioxaphosphorinanes with polyfluorinated alcohols. Principal chemical properties of the products were studied. For the first time copper complexes of fluorine-containing normal phosphites were prepared. A difference in the ligation of copper with fluorinated and nonfluorinated phosphites was shown.

Polyfluoroalkyl esters of trivalent phosphorus acids often exibit specific chemical properties and therefore are actively studied [1]. At the same time, phosphocyclic systems containing polyfluorinated exocyclic substituents have not yet considered as a separate group of compounds. Therefore, we set ourselves the task to study their synthesis and chemical properties.

We found that 2-polyfluoroalkoxy-1,3,2-dioxaphosphorinanes are readily and effectively available by the reaction of the corresponding cyclic phosphamides with polyfluoroalkanols.

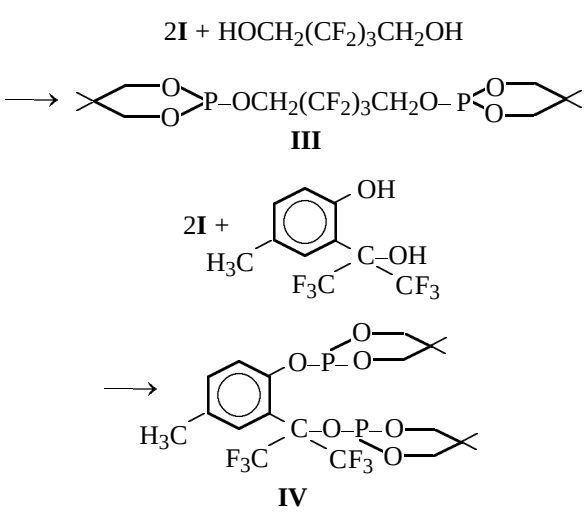


I **II**

Analogous reaction also proceeds with 2-diethylamino-4-methyl-1,3,2-dioxaphosphorinanes, but it most frequently leads to a mixture of geometric isomers with different spectral characteristics. Note that in benzene this reaction selectively provides only one geometric isomer. It is important that the facility of the alcoholysis is always dependent on the degree of fluorination of the starting alcohols. Hence, the alcoholysis with trifluoromethylethanol is almost twice as slow as with hexafluorodimethylcarbinol.

We also prepared diphosphites **III** and **IV** on the basis of fluorinated diols, 2,2,3,3,4,4-hexafluoropentane-1,5-diol and 2-[2,2,2-trifluoro-1-(trifluoromethyl)-1-hydroxyethyl]-4-methylphenol.

The fluorine-containing phosphites and diphosphites were brought into oxidation and sulfurization reactions to obtain the corresponding phosphates and phosphorothioates. It is interesting to note that di-



III **IV**

phosphite **IV** under usual conditions takes up only one sulfur atom, probably, by a more electron-donor phosphorus atom.

At present much interest is being shown in the synthesis, structure, and catalytic acivity of copper(I) phosphite complexes. The complex formation is found to the affected by the nature of the phosphite ligand [2]. We prepared copper complexes of cyclophosphite $C_{28}H_{60}Br_4Cu_4O_{12}P_4$ (**V**) and fluorinated cyclophosphite $C_{18}H_{302}BrCuF_9O_9P_3$ (**VI**). It was found that complex **V** has a standard cubic structure of the inner fragment $[Cu_4Br_4]$ with the four phosphite ligands in the *chair* conformation, exported on the periphery. Complex **VI** is tetrahedral with a slightly distorted coordination: The angles at the Cu^1 atom vary from 106.35(8) to 121.4(1)° (see Figs. 1 and 2).

The six-membered phosphorus-containing heterorings have the *chair* conformation, with the mean

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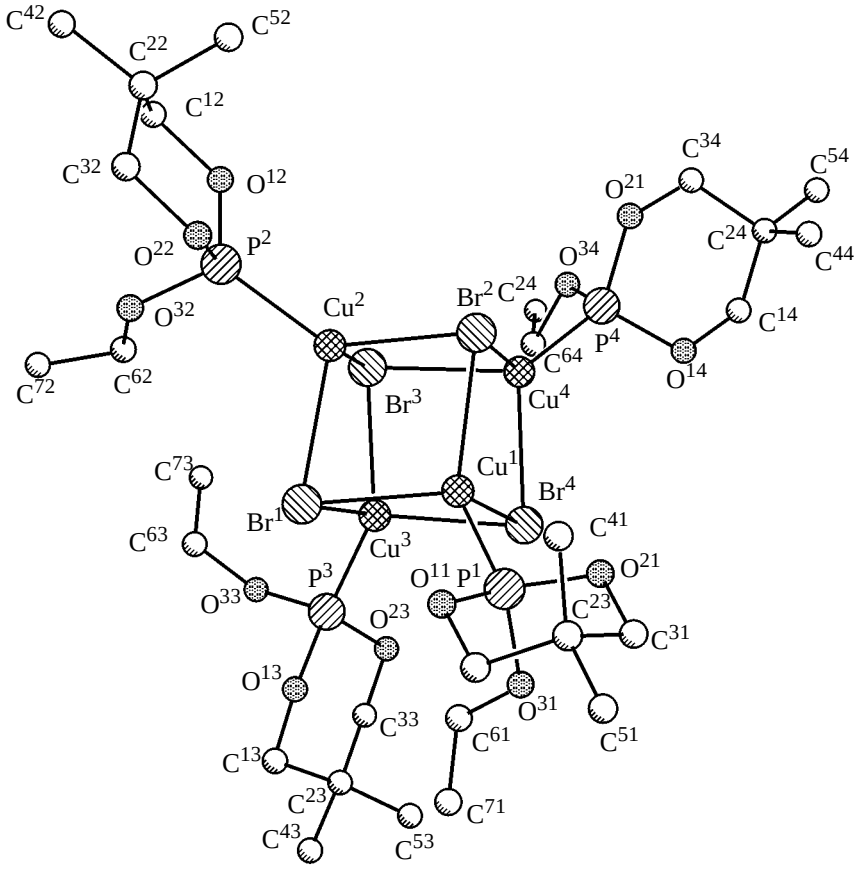

Fig. 1. General view of molecule **V** and the atom numbering scheme.

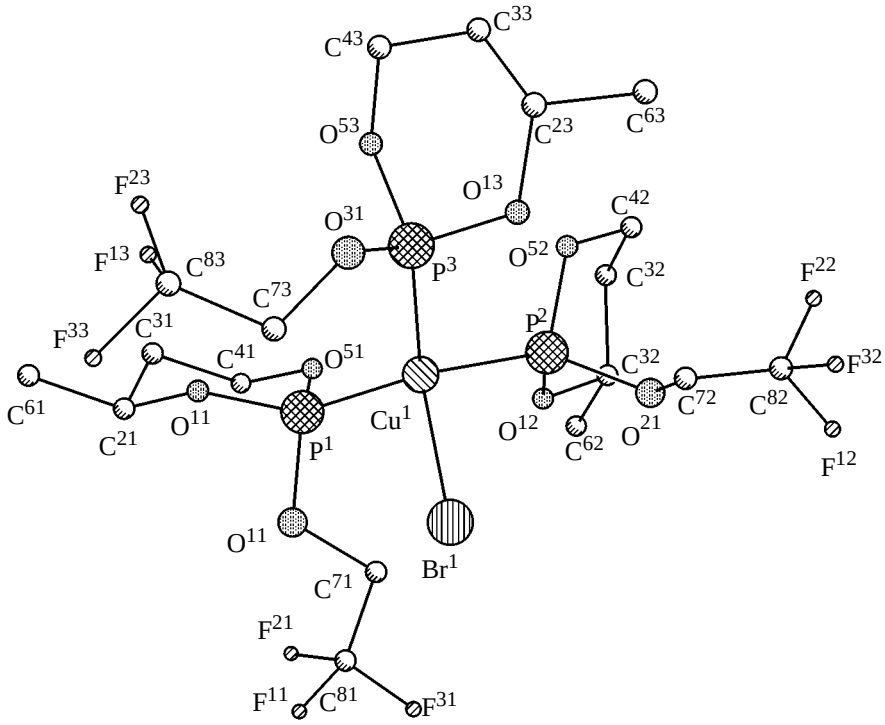

Fig. 2. General view of molecule **VI** and the atom numbering scheme.

deviation of the phosphorus atoms fom the ring planes of 0.56 Å.

It is evident that fluoroalkyl cyclophosphite coordination systems may present interest as catalysts for reactions in which electron-acceptor ligands enhance the catalytic activity of the complexes.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded on a Bruker WP-80SY instrument (80 MHz). The ^{1}H NMR spectra were obtained on a Bruker AM250 spectrometer (250 MHz). The chemical shifts are measured against internal HMDS (^{1}H) and external 85% phosphoric acid (^{31}P).

All the syntheses were carried under dry nitrogen in absolute solvents.

The reaction progress was followed and the individuality of the products was controlled by TLC on Silufol plates, elution with 14:1 hexane–dioxane (A), 3:1 benzene–dioxane (B), 1:1 benzene–dioxane (C), 3:1 hexane–dioxane (D), 5:1 benzene–dioxane (E), and 3:1 chloroform–methanol (F).

The X-ray diffraction analysis of single crystals of **V** and **VI** was performed on a Siemens P3/Pc automatic four-circle diffractometer (MoK_α radiation, graphite monochromator, θ/2θ scanning, 2θ<48°). Crystal data for compound **V**, $C_{28}H_{60}Br_4Cu_4O_{12}P_4$: monoclinic; at –120°C, *a* 11.593(4) Å, *b* 20.490(3) Å, *c* 40.712(7) Å, β 95.47(2) Å, *V* 9627(3) Å^3, *Z* = 8, μ 5.245 μm^{-1}, *F*(000) 5120, d_{calc} 1.775 g/cm^3, *M* 1286.44, space group *C*2*c*. Of 7123 measured reflections, 6808 unique ones were used in further calculations and refinment. Final divergence factors: *wR*2 0.1987, *GOF* 0.983, on all reflections; *R*1 0.0608, on 3788 reflections with $I > 2\sigma(I)$, refinment on *F*. The atomic coordinates and thermal parameters are listed in Table 1, and the bond lengths and angles are given in Table 2.

Crystal data for complex **VI**, $C_{18}H_{30}BrCuF_9O_9P_3$: monoclinic; at 25°C, *a* 14.020(4) Å, *b* 16.254(5) Å, *c* 14.866(4) Å, *V* 3223(2), *Z* 4, μ 2.144 mm^{-1}, *F*(000) 1600, d_{calc} 1.620 g/cm^3, *M* 785.94, space group *P*21/*n*. Of 4546 measured reflections, 4100 unique ones were used in further calculations and refinement. Final divergence factors: *wR*2 0.2013, on all the 4100 reflections; *R*1 0.0769, *GOF* 1.032, on 3542 reflections with $I > 2\sigma$. The coordinates of non-hydrogen atoms and their equivalent isotropic thermal parameters are listed in Table 3, and the bond lengths and angles are given in Table 4.

The structures were solved by the direct method and refined in anisotropic–isotropic full-matrix approximation on *F*. Analysis of the residual electron density showed that the ethyl group on O(33) in compound **V** is disordered over two positions with occupancies of 0.5. The positions of hydrogen atoms were calculated from geometric considerations and refined by the rider model. All the calculations were carried out on an IBM PC/AT computer by means of the SHELXTL PLUS 5.0 program complex. Absorption was considered by means of the DIFABS program [3].

2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]-5,5-dimethyl-1,3,2-dioxaphosphorinane (II). 2-Diethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane (**I**), 3 g, and 2.48 g of 2,2,2-trifluoro-1-(trifluoromethyl)ethanol were dissolved in absolute benzene, and the solution was left to stand at room temperature for 48 h. The solvent was then removed in a vacuum, and the residue was distilled. Yield 57%, bp 26–28°C (20 mm), R_f 0.8 (A). ^{31}P NMR spectrum: δ_P 125.1 ppm. ^{1}H NMR spectrum, δ, ppm: 0.13 (CH_3^e, 3H), 0.45 (CH_3^a, 3H), 3.03 (CH^e, 1H), 3.92 (CH^a, 1H), 4.13 (CH, 1H). Found, %: C 32.16, H 3.45, P 10.30. $C_8H_{11}F_6PO_3$. Calculated, %: P C 32.00, H 3.66, C 10.30.

2,2,3,3,4,4-Hexafluoro-1,5-bis(5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy)pentane (III). A solution of 3.8 g of 2,2,3,3,4,4,-hexafluoropentane-1,5-diol in 10 ml of absolute dioxane and 5.4 ml of anhydrous triethylamine were added dropwise to a solution of 5.18 ml of 2,2-dimethyltrimethylene phosphorochloridite in 100 ml of absolute dioxane. The reaction mixture was stirred for 1.5 h with cooling. The triethylamine hydrochloride was filtered off, the solvent was removed, and the residue was distilled in a high vacuum. Yield 70%, bp 125°C (10^{-4} mm). R_f 0.84 (D) and 0.82 (C). ^{31}P NMR spectrum: δ_P 123.4 ppm. ^{1}H NMR spectrum, δ, ppm: 0.2 (CH_3^e, 6H), 1.04 (CH_3^a, 6H), 3.07 (CH_2^e, 4H), 4.02 (CH_2^a, 4H), 4.04 (CH_2, 4H). Found, %: C 38.04, H 4.92, P 13.75. $C_{15}H_{24}F_6P_2O_6$. Calculated, %: C 37.82, H 5.04, P 13.02.

2-[2,2,2-Trifluoro-1-(trifluoromethyl)-1-[5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]ethyl]-4-methyl-1-(5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy)benzene (IV). A solution of 1.8 g of 2-[2,2,2-trifluoro-1-(trifluoromethyl)-1-hydroxyethyl]-4-methylphenol in 10 ml of absolute benzene and 2 ml of triethylamine were added dropwise to a solution of 1.5 ml of 2,2-dimethyltrimethylene phosphorochloridite in 100 ml of absolute benzene. The reaction mixture was stirred with cooling for 2 h, the triethylamine hydrochloride was filtered off, the solvent was

Table 1. Coordinates of non-hydrogen atoms (10^4) and their equivalent isotropic thermal parameters ($Å^2 \times 10^3$) in complex **V**

Atom	*x*	*y*	*z*	*U*	Atom	*x*	*y*	*z*	*U*
Br^1	225(1)	–5179(1)	1523(1)	69(1)	C^{52}	–493(14)	–7710(8)	267(3)	148(7)
Br^2	1732(1)	–5237(1)	721(1)	63(1)	C^{62}	52(16)	–7181(8)	1691(4)	137(6)
Br^3	3033(1)	–6163(1)	1490(1)	75(1)	C^{72}	–634(17)	–7525(11)	1906(4)	175(8)
Br^4	3311(1)	–4310(1)	1453(1)	68(1)	P^3	2511(3)	–5036(2)	2302(1)	80(1)
Cu^1	1190(1)	–4447(1)	1138(1)	74(1)	O^{13}	1547(7)	–4611(6)	2443(2)	123(4)
Cu^2	1115(1)	–6014(1)	1149(1)	71(1)	O^{23}	36(47)	–4677(5)	2453(2)	108(3)
Cu^3	2345(1)	–5166(1)	1772(1)	80(1)	O^{33}	2520(12)	–5669(5)	2528(2)	149(5)
Cu^4	3621(1)	–5220(1)	1067(1)	75(1)	C^{13}	1665(12)	–4404(9)	2789(3)	122(6)
P^1	407(2)	–3487(1)	1079(1)	58(1)	C^{23}	2782(13)	–4071(8)	2872(3)	94(4)
O^{11}	–954(5)	–3501(3)	1034(2)	63(2)	C^{33}	3760(13)	–4489(9)	2795(3)	116(5)
O^{21}	742(5)	–3049(3)	782(2)	65(2)	C^{43}	2909(15)	–3932(8)	3263(3)	134(6)
O^{31}	731(8)	–2985(4)	1370(2)	95(3)	C^{53}	2799(20)	–3421(10)	2697(4)	203(11)
C^{11}	–1565(8)	–2882(5)	953(3)	71(3)	C^{63}	1665(20)	–6147(13)	2421(9)	151(13)
C^{21}	–1192(8)	2580(5)	649(2)	54(2)	C^{73}	2562(47)	–6709(27)	2401(16)	402(49)
C^{31}	81(8)	–2449(5)	699(3)	66(3)	$C^{63'}$	3348(24)	–6142(17)	2442(13)	209(22)
C^{41}	–1469(11)	–3019(6)	355(3)	89(4)	$C^{73'}$	4601(36)	–6157(32)	2618(17)	482(65)
C^{51}	–1805(9)	–1928(5)	586(3)	74(3)	P^4	5322(2)	–5396(1)	900(1)	58(1)
C^{61}	728(19)	–3204(9)	1697(4)	155(8)	O^{14}	6138(6)	–4776(3)	905(2)	69(2)
C^{71}	479(22)	–2798(12)	1923(5)	209(10)	O^{24}	5396(5)	–5687(3)	542(2)	57(2)
P^2	49(2)	–6875(1)	1068(1)	60(1)	O^{34}	6070(6)	–5939(4)	1101(2)	80(2)
O^{12}	672(5)	–7503(3)	950(2)	76(2)	C^{14}	7253(9)	–4844(6)	780(3)	75(3)
O^{22}	–1072(6)	–6818(3)	813(2)	79(2)	C^{24}	7141(8)	–5090(5)	431(3)	59(3)
O^{32}	–633(7)	–7108(5)	1374(2)	99(3)	C^{34}	6515(9)	–5725(5)	423(3)	64(3)
C^{12}	–4(9)	–8096(5)	857(3)	80(4)	C^{44}	6496(11)	–4631(6)	189(3)	89(4)
C^{22}	–976(8)	–7942(5)	595(2)	60(3)	C^{54}	8373(10)	–5203(6)	328(3)	97(4)
C^{32}	–1739(8)	–7415(6)	721(3)	78(3)	C^{64}	6261(14)	–5910(12)	1454(4)	171(9)
C^{42}	–1722(9)	–8552(5)	530(3)	73(3)	C^{74}	7145(17)	–6179(11)	1590(3)	201(11)

removed, and the residue was distilled in a high vacuum. Yield 62%, bp 140°C (10^{-4} mm). R_f 0.8 (B) and 0.65 (C). ^{31}P NMR spectrum, δ_P, ppm: 121.8, 110.0. ^1H NMR spectrum, δ, ppm: 0.3 (CH_3^e, H), 0.6 (CH_3^a, H), 0.6 (CH_3^e, H), 1.1 (CH_3^a, H), 1.8 (H, CH_{3arom}), 3.2 (H^e), 3.7 (H^e), 3.9 (H^a), 4.2 (H^a), 6.8 ($2H_{arom}$), 7.2 (H_{arom}). Found.%: C 33.42, H 4.63, P 11.28. $C_{20}H_{26}F_6P_2O_6$. Calculated, %: C 33.17, H 4.57, P 11.32.

2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane 2-sulfide. A mixture of 0.5 g of fluorinated phosphite **II** and 0.05 g of sulfur in 5 ml of absolute dioxane was heated in a sealed ampule at 130–135°C for 10 h. The resulting light yellow powder was filtered off and purified by crystallization from dioxane. Yield 48%. mp 112–114°C. R_f 0.8 (E). ^{31}P NMR spectrum: δ_P 60.3 ppm. ^1H NMR spectrum, δ, ppm: 0.02 (CH_3^e, 3H), 0.08 (CH_3^a, 3H), 3.32 (CH^e, 1H), 3.64 (CH^a, 1H), 5.48 (CH, 1H). Found, %: C 28.95, H 3.26, P 9.37. $C_8H_{11}F_6PO_3S$. Calculated, %: C 28.92, H 3.31, P 9.34.

2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane 2-oxide. Iodosobenzene, 0.4 g, was added in portions to a solution of 0.2 g of fluorinated phosphite **II** in absolute benzene. The reaction mixture was left to stand at room temperature for 24 h, and unreacted iodosobenzene was then filtered off. The solvent was removed to leave colorless crystals. They were washed with several portions of hexane and dried in a vacuum (1 mm). Yield 50%, mp 79–80°C. R_f 0.5 (F). ^{31}P NMR spectrum: δ_P –10.3 ppm. Found, %: C 30.43, H 3.51, P 9.59. $C_8H_{11}F_6PO_4$. Calculated, %: C 30.38, H 3.48, P 9.81.

2,2,3,3,4,4-Hexafluoro-1,5-bis(5,5-dimethyl-2-thioxo-1,3,2λ^5-dioxaphosphorinan-2-yloxy)pentane. A mixture of 0.7 g of compound **III** and 0.1 g of sulfur in 5 ml of absolute dioxane were heated for 6 h

Table 2. Bond lengths (Å) and bond angles (deg) in complex **V**

Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
Br^1–Cu^1	2.507(2)	O^{22}–C^{32}	1.476(12)	Cu^4–P^4	2.177(3)	C^{23}–C^{33}	1.48(2)
Br^1–Cu^3	2.568(2)	O^{32}–C^{62}	1.46(2)	P^1–O^{11}	1.571(6)	C^{23}–C^{53}	1.51(2)
Br^1–Cu^2	2.572(2)	C^{12}–C^{22}	1.510(14)	P^1–O^{31}	1.586(8)	C^{23}–C^{43}	1.61(2)
Br^2–Cu^1	2.471(2)	C^{22}–C^{32}	1.515(14)	P^1–O^{21}	1.584(7)	C^{63}–C^{73}	1.560(2)
Br^2–Cu^4	2.488(2)	C^{22}–C^{42}	1.527(13)	O^{11}–C^{11}	1.476(11)	$C^{63'}$–$C^{73'}$	1.559(12)
Br^2–Cu^2	2.513(2)	C^{22}–C^{52}	1.57(2)	O^{21}–C^{31}	1.470(11)	P^4–O^{24}	1.587(6)
Br^3–Cu^3	2.511(2)	C^{62}–C^{72}	1.42(2)	O^{31}–C^{61}	1.40(2)	P^4–O^{14}	1.583(7)
Br^3–Cu^2	2.526(2)	P^3–O^{13}	1.567(9)	C^{11}–C^{21}	1.485(13)	P^4–O^{34}	1.587(8)
Br^3–Cu^4	2.720(2)	P^3–O^{23}	1.580(9)	C^{21}–C^{31}	1.494(12)	O^{14}–C^{14}	1.442(12)
Br^4–Cu^4	2.488(2)	P^3–O^{33}	1.588(10)	C^{21}–C^{41}	1.509(14)	O^{24}–C^{34}	1.428(11)
Br^4–Cu^3	2.508(2)	O^{13}–C^{13}	1.467(14)	C^{21}–C^{51}	1.523(13)	O^{34}–C^{64}	1.44(2)
Br^4–Cu^1	2.677(2)	O^{23}–C^{33}	1.440(13)	C^{61}–C^{71}	1.29(2)	C^{14}–C^{24}	1.498(14)
Cu^1–P^1	2.171(3)	O^{33}–$C^{63'}$	1.429(11)	P^2–O^{12}	1.571(7)	C^{24}–C^{34}	1.487(13)
Cu^2–P^2	2.162(3)	O^{33}–C^{63}	1.430(11)	P^2–O^{22}	1.587(7)	C^{24}–C^{44}	1.510(14)
Cu^3–P^3	2.165(3)	C^{13}–C^{23}	1.47(2)	P^2–O^{32}	1.610(8)	C^{24}–C^{54}	1.545(14)
				O^{12}–C^{12}	1.477(12)	C^{64}–C^{74}	1.54(2)
Angle	ω	Angle	ω	Angle	ω	Angle	ω
$Cu^1Br^1Cu^3$	76.91(6)	$O^{12}P^2O^{32}$	105.5(5)	$Br^4Cu^3Br^1$	105.09(6)	$C^{33}C^{23}C^{13}$	110.9(13)
$Cu^1Br^1Cu^2$	78.43(6)	$O^{22}P^2O^{32}$	95.4(5)	$Br^3Cu^3Br^1$	98.30(6)	$C^{33}C^{23}C^{53}$	111.4(14)
$Cu^3Br^1Cu^2$	79.54(5)	$O^{12}P^2Cu^2$	116.2(3)	$P^4Cu^4Br^2$	126.58(10)	$C^{13}C^{23}C^{53}$	111(2)
$Cu^1Br^2Cu^4$	82.48(6)	$O^{22}P^2Cu^2$	117.4(3)	$P^4Cu^4Br^4$	120.77(10)	$C^{33}C^{23}C^{43}$	108.2(12)
$Cu^1Br^2Cu^2$	80.24(6)	$O^{32}P^2Cu^2$	116.1(3)	$Br^2Cu^4Br^4$	101.32(6)	$C^{13}C^{23}C^{43}$	107.8(11)
$Cu^4Br^2Cu^2$	84.82(6)	$C^{12}O^{12}P^2$	120.2(6)	$P^4Cu^4Br^3$	111.66(10)	$C^{53}C^{23}C^{43}$	107.9(12)
$Cu^3Br^3Cu^2$	81.49(6)	$C^{32}O^{22}P^2$	118.8(7)	$Br^2Cu^4Br^3$	95.09(6)	$O^{23}C^{33}C^{23}$	11.0(11)
$Cu^3Br^3Cu^4$	79.69(6)	$C^{12}O^{32}P^2$	116.7(9)	$Br^4Cu^4Br^3$	94.08(6)	$O^{33}C^{63}C^{73}$	94(3)
$Cu^2Br^3Cu^4$	79.93(5)	$O^{32}C^{12}C^{22}$	110.6(9)	$O^{11}P^1O^{31}$	105.3(5)	$O^{33}C^{63'}C^{73'}$	121(4)
$Cu^4Br^4Cu^3$	84.40(6)	$C^{62}C^{22}C^{42}$	107.7(8)	$O^{11}P^1O^{21}$	103.8(4)	$O^{24}P^4O^{14}$	103.3(4)
$Cu^4Br^4Cu^1$	78.44(5)	$C^{12}C^{22}C^{12}$	109.4(9)	$O^{31}P^1O^{21}$	98.5(4)	$O^{24}P^4O^{34}$	97.8(4)
$Cu^3Br^4Cu^1$	74.94(5)	$C^{32}C^{22}C^{12}$	108.9(9)	$O^{11}P^1Cu^1$	113.6(3)	$O^{14}P^4O^{34}$	105.1(4)
$P^1Cu^1Br^2$	130.48(10)	$C^{32}C^{22}C^{52}$	109.8(11)	$O^{31}P^1Cu^1$	116.0(3)	$O^{24}P^4Cu^4$	118.6(3)
$P^1Cu^1Br^1$	113.83(10)	$C^{42}C^{22}C^{52}$	109.9(9)	$O^{21}P^1Cu^1$	117.8(3)	$O^{14}P^4Cu^4$	114.9(3)
$Br^2Cu^1Br^1$	101.29(6)	$C^{32}C^{22}C^{52}$	11.2(10)	$C^{11}O^{11}P^1$	117.7(6)	$O^{34}P^4Cu^4$	115.0(3)
$P^1Cu^1Br^4$	108.24(9)	$O^{42}C^{32}C^{22}$	111.6(7)	$C^{31}O^{21}P^1$	119.2(6)	$C^{14}O^{14}P^4$	118.1(6)
$Br^2Cu^1Br^4$	96.68(6)	$C^{12}C^{62}O^{32}$	107.8(14)	$C^{61}O^{31}P^1$	118.7(10)	$C^{34}O^{24}P^4$	117.5(6)
$Br^1Cu^1Br^4$	101.95(6)	$O^{22}P^3O^{23}$	101.3(5)	$O^{11}C^{11}C^{21}$	111.9(8)	$C^{64}O^{34}P^4$	120.8(10)
$P^2Cu^2Br^2$	127.43(10)	$O^{72}P^3O^{33}$	102.1(7)	$C^{11}C^{21}C^{31}$	108.8(8)	$O^{14}C^{14}C^{24}$	111.6(8)
$P^2Cu^2Br^3$	116.44(10)	$O^{13}P^3O^{33}$	101.4(6)	$C^{11}C^{21}C^{41}$	110.9(9)	$C^{14}C^{24}C^{34}$	108.3(9)
$Br^2Cu^2Br^3$	99.50(6)	$O^{13}P^3Cu^3$	115.6(4)	$C^{31}C^{21}C^{41}$	110.3(9)	$C^{14}C^{24}C^{44}$	113.7(10)
$P^2Cu^2Br^1$	112.19(10)	$O^{23}P^3Cu^3$	115.9(3)	$C^{11}C^{21}C^{51}$	109.7(8)	$C^{34}C^{24}C^{44}$	108.7(9)
$Br^2Cu^2Br^1$	98.40(6)	$O^{33}P^3Cu^3$	118.1(4)	$C^{31}C^{21}C^{51}$	107.7(8)	$C^{14}C^{24}C^{54}$	108.0(9)
$Br^3Cu^2Br^1$	97.80(6)	$C^{13}O^{13}P^3$	120.4(9)	$C^{41}C^{21}C^{51}$	109.2(9)	$C^{34}C^{24}C^{54}$	109.0(9)
$P^3Cu^3Br^4$	115.38(12)	$C^{33}O^{23}P^3$	119.8(8)	$O^{21}C^{31}C^{21}$	111.6(8)	$C^{44}C^{24}C^{54}$	109.1(9)
$P^3Cu^3Br^3$	123.59(12)	$C^{63'}O^{33}P^3$	112(2)	$C^{71}C^{61}O^{31}$	119(2)	$O^{24}C^{34}C^{24}$	113.7(8)
$Br^4Cu^3Br^3$	98.95(6)	$C^{63}O^{33}P^3$	115(2)	$O^{12}P^2O^{22}$	103.5(4)	$C^{74}C^{64}O^{34}$	118(2)
$P^3Cu^3Br^1$	112.75(11)	$O^{13}C^{13}C^{23}$	110.8(11)				

Table 3. Coordinates of non-hydrogen atoms (10^4) and their equivalent isotropic thermal parameters ($Å \times 10^3$) in complex **VI**

Atom	*x*	*y*	*z*	*U*
Cu^1	5798(1)	–3971(1)	–2143(1)	49(1)
Br^1	6952(1)	–4059(1)	–539(1)	75(1)
P^1	6544(2)	–4608(2)	–3072(2)	49(1)
P^2	5594(2)	–2639(2)	–2537(2)	52(1)
P^3	4350(2)	–4418(2)	–2006(2)	57(1)
O^{11}	7755(5)	–4598(4)	–2706(5)	63(2)
O^{21}	5813(5)	–1958(4)	–1693(5)	68(2)
O^{31}	4307(9)	–5172(7)	–1340(7)	116(3)
F^{11}	9694(7)	–4513(7)	–1588(10)	183(5)
F^{21}	9562(9)	–4222(10)	–2913(11)	205(6)
F^{31}	9834(5)	–3281(5)	–1874(7)	125(3)
F^{12}	5880(16)	–755(8)	–433(12)	228(7)
F^{22}	4533(15)	–918(11)	–1216(13)	250(8)
F^{32}	4882(13)	–1368(7)	–138(9)	196(6)
F^{13}	4672(13)	–6459(8)	–2434(8)	195(5)
F^{23}	3979(12)	–6870(7)	–1504(10)	198(5)
F^{33}	5484(14)	–7123(7)	–1217(13)	237(7)
C^{11}	6393(5)	–5555(4)	–3251(5)	29(2)
C^{12}	6295(6)	–2275(5)	–3071(5)	35(2)
C^{13}	3847(6)	–3754(6)	–1530(7)	51(2)
C^{21}	6782(8)	–5980(7)	–3933(8)	72(3)
C^{22}	6108(12)	–1446(7)	–3537(8)	87(3)
C^{23}	2774(11)	–3795(16)	–1583(14)	154(7)
C^{31}	6395(11)	–5536(9)	–4856(8)	96(4)
C^{32}	5025(14)	–1447(9)	–4140(10)	120(5)
C^{33}	2168(10)	–4078(18)	–2635(15)	164(8)
C^{41}	6688(14)	–4640(10)	–4797(9)	111(5)
C^{42}	4296(12)	–1611(10)	–3600(11)	120(5)
C^{43}	2510(13)	–4776(20)	–2925(15)	183(10)
C^{51}	6307(7)	–4238(5)	–4098(5)	40(2)
C^{52}	4496(6)	–2413(5)	–3190(6)	49(2)
C^{53}	3468(7)	–4614(9)	–2938(6)	75(4)
C^{62}	6892(16)	–1356(10)	–4021(11)	132(6)
C^{61}	6454(14)	–6853(9)	–3921(15)	150(7)
C^{63}	2527(14)	–2976(18)	–1318(16)	200(10)
C^{71}	8256(8)	–3847(7)	–2352(10)	81(3)
C^{72}	5420(12)	–2089(8)	–920(10)	96(4)
C^{73}	5028(15)	–5756(9)	–1059(10)	115(5)
C^{81}	9326(9)	–3965(9)	–2188(11)	90(3)
C^{82}	4813(17)	–6557(10)	–1536(12)	124(5)
C^{83}	5167(19)	–1351(10)	–599(14)	136(5)

in a sealed ampule at 100–105°C. The resulting light yellow powder was filtered off and washed with benzene. Yield 47%, mp 114°C, R_f 0.63 (D). ^{31}P NMR spectrum: δ_P 60.2 ppm. ^1H NMR spectrum, δ, ppm: 0.1 (CH_3^e, 3H), 0.74 (CH_3^a, 6H), 3.03 (CH_2^e, 4H), 3.7 (CH_2^a, 4H), 4.38 (CH_2, 4H); $J_{H^aH^e}$ 10.67 Hz, J_{CH_2P}

Table 4. Bond lengths (Å) and bond angles (deg) in complex **VI**

Bond	*d*	Bond	*d*
Cu^1–P^3	2.223(3)	F^{13}–C^{83}	1.30(2)
Cu^1–P^1	2.228(3)	F^{23}–C^{83}	1.29(2)
Cu^1–P^2	2.237(3)	F^{33}–C^{83}	1.30(2)
Cu^1–Br^1	2.439(2)	C^{11}–C^{21}	1.46(1)
P^1–C^{11}	1.566(7)	C^{12}–C^{22}	1.50(1)
P^1–C^{51}	1.577(8)	C^{13}–C^{23}	1.48(2)
P^1–O^{11}	1.616(7)	C^{21}–C^{61}	1.49(2)
P^2–C^{12}	1.557(7)	C^{21}–C^{31}	1.50(2)
P^2–C^{52}	1.590(8)	C^{22}–C^{62}	1.50(2)
P^2–O^{21}	1.630(7)	C^{22}–C^{32}	1.51(2)
P^3–C^{13}	1.570(9)	C^{23}–C^{63}	1.46(3)
P^3–C^{53}	1.580(9)	C^{23}–C^{33}	1.60(3)
P^3–O^{31}	1.589(9)	C^{31}–C^{41}	1.51(2)
O^{11}–C^{71}	1.436(1)	C^{32}–C^{42}	1.50(2)
O^{21}–C^{72}	1.44(1)	C^{33}–C^{43}	1.35(3)
O^{31}–C^{73}	1.36(2)	C^{41}–C^{51}	1.46(1)
F^{11}–C^{81}	1.25(2)	C^{42}–C^{52}	1.43(2)
F^{21}–C^{81}	1.29(2)	C^{43}–C^{53}	1.39(2)
F^{31}–C^{81}	1.32(1)	C^{71}–C^{81}	1.46(2)
F^{12}–C^{82}	1.36(3)	C^{72}–C^{82}	1.38(2)
F^{22}–C^{82}	1.27(2)	C^{73}–C^{83}	1.47(2)
F^{32}–C^{82}	1.28(2)		
Angle	**ω**	**Angle**	**ω**
$P^3Cu^1P^1$	121.4(1)	$C^{12}C^{22}C^{32}$	106(1)
$P^3Cu^1P^2$	107.1(1)	$C^{63}C^{23}C^{13}$	105(2)
$P^1Cu^1P^2$	109.5(1)	$C^{63}C^{23}C^{33}$	115(2)
$P^3Cu^1Br^1$	103.94(9)	$C^{13}C^{23}C^{33}$	107(1)
$P^1Cu^1Br^1$	106.35(8)	$C^{21}C^{31}C^{41}$	113(1)
$P^2Cu^1Br^1$	107.79(8)	$C^{22}C^{32}C^{42}$	114(1)
$C^{11}P^1C^{51}$	103.5(4)	$C^{43}C^{33}C^{23}$	115(2)
$C^{11}P^1O^{11}$	98.1(4)	$C^{51}C^{41}C^{31}$	109(1)
$C^{51}P^1O^{11}$	102.0(4)	$C^{52}C^{42}C^{32}$	108(1)
$C^{11}P^1Cu^1$	119.8(3)	$C^{33}C^{43}C^{53}$	106(2)
$C^{51}P^1Cu^1$	115.0(3)	$C^{41}C^{51}P^1$	120.2(8)
$O^{11}P^1Cu^1$	115.6(3)	$C^{42}C^{52}P^2$	119.8(9)
$C^{12}P^2C^{52}$	104.2(5)	$C^{43}C^{53}P^3$	122(1)
$C^{12}P^2O^{21}$	97.8(4)	$O^{11}C^{71}C^{81}$	108(1)
$C^{52}P^2O^{21}$	103.3(5)	$C^{82}C^{72}O^{21}$	111(1)
$C^{12}P^2Cu^1$	116.9(3)	$O^{31}C^{73}C^{83}$	117(2)
$C^{52}P^2Cu^1$	113.9(3)	$F^{11}C^{81}F^{21}$	102(1)
$O^{21}P^2Cu^1$	118.5(3)	$F^{11}C^{81}F^{31}$	106(1)
$C^{13}P^3C^{53}$	101.2(6)	$F^{21}C^{81}F^{31}$	108(1)
$C^{13}P^3O^{31}$	98.1(6)	$F^{11}C^{81}C^{71}$	112(1)
$C^{53}P^3O^{31}$	102.8(6)	$F^{21}C^{81}C^{71}$	115(1)
$C^{13}P^3Cu^1$	111.4(3)	$F^{31}C^{81}C^{71}$	111(1)
$C^{53}P^3Cu^1$	118.4(3)	$F^{23}C^{83}F^{13}$	104(2)
$C^{31}P^3Cu^1$	121.4(4)	$F^{23}C^{83}F^{33}$	106(2)

Table 4. (Contd.)

Angle	ω	Angle	ω
$C^{71}O^{11}P^{1}$	118.7(6)	$F^{13}C^{83}F^{33}$	109(2)
$C^{72}O^{21}P^{2}$	119.2(7)	$F^{23}C^{83}C^{73}$	113(2)
$C^{73}O^{31}P^{3}$	124.3(10)	$F^{13}C^{83}C^{73}$	109(1)
$C^{21}C^{11}P^{1}$	121.4(7)	$F^{33}C^{83}C^{73}$	116(2)
$C^{22}C^{12}P^{2}$	121.9(8)	$F^{32}C^{82}F^{22}$	107(2)
$C^{23}C^{13}P^{3}$	122.2(11)	$F^{32}C^{82}F^{12}$	105(2)
$C^{11}C^{21}C^{61}$	105.0(11)	$F^{22}C^{82}F^{12}$	93(2)
$C^{11}C^{21}C^{31}$	107.5(9)	$F^{32}C^{82}C^{72}$	118(1)
$C^{61}C^{21}C^{31}$	116.3(12)	$F^{22}C^{82}C^{72}$	115(2)
$C^{62}C^{22}C^{12}$	105.1(12)	$F^{12}C^{82}C^{72}$	116(2)
$C^{62}C^{22}C^{32}$	118.0(12)		

9.39 Hz, J_{CH_2F} 13.66 Hz, J_{H^aP} 4.47 Hz, J_{H^eP} 22.63 Hz. Found, %: C 33.33, H 4.37, P 11.48. $C_{15}H_{24}F_6O_6P_2S_2$. Calculated, %: C 33.75, H 4.02, P 11.28.

2-[2,2,2-Trifluoro-1-(trifluoromethyl)-1-[5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]ethyl]-4-methyl-1-(5,5-dimethyl-2-thioxo-1,3,2λ^5-dioxaphosphorinan-2-yloxy)benzene. A mixture of 1 g of compound **IV** and 1.12 g of sulfur in 5 ml of absolute dioxane was heated for 7 h in a sealed ampule at 100–105°C. The resulting precipitate was filtered off, dissolved in benzene, and crystallized in the cold to obtain an amorphous white powder which was washed with dioxane. Yield 24%, mp 132°C, R_f 0.83 (B) and 0.61 (C). ^{31}P NMR spectrum: δ_P 110.2 and 61.9 ppm. ^{1}H NMR spectrum, δ, ppm: 0.2 (CH_3^e, H), 0.6 (CH_3^a), 0.6 (CH_3^e, H), 1.01 (CH_3^a, H), 1.9 (CH_{3arom}, H), 3.3 (H^e), 3.4 (H^e), 3.6 (H^a), 4.1 (H^a), 7.03 (H_{arom}). Found, %: C 37.02, H 4.58, P 11.23. $C_{20}H_{26}O_6P_2S_2$. Calculated, %: C 36.87, H 4.43, P 11.13.

Copper complex V. A mixture of 2 g of 2-ethoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane and 1.77 g of copper(I) bromide in absolute benzene was kept at room temperature for 24 h under dry nitrogen. Then the reaction mixture was filtered, the solvent was evaporated until almost dryness, and the product was crystallized from benzene. Yield 47%. ^{31}P NMR spectrum: δ_P 97 ppm. Coordination shift 25 ppm. $C_{28}H_{60} \cdot Br_4Cu_4O_{12}P_4$.

Copper complex VI. A mixture of 1.2 g of 2-(2,2,2-trifluoroethoxy)-4-methyl-1,3,2-dioxaphosphorinane and 0.5 g of copper(I) bromide in 10 ml of absolute benzene was kept at room temperature for 24 h under dry nitrogen. Then the reaction mixture was filtered off, the solvent was evaporated until almost dry, and the product was crystallized from benzene. Yield 68%, mp 102°C, R_f 0.72 (C). ^{31}P NMR spectrum: δ_P 112.5 ppm. Coordination shift 6.5 ppm. $C_{18}H_{30}BrCuF_9O_9P_3$.

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