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To the 80th Anniversary of B.I. Ionin

Caged Phosphorane with P–C Bond Based on Chloral and 4,5-Dimethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane

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Abstract—The key methods of caged phosphoranes synthesis are analyzed. Reaction of 4,5-dimethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane (prepared from the *meso*-form of 2,3-butanediol) with chloral has yielded the caged phosphorane containing a phosphorus–carbon bond: 1,1-(1,2-dimethylethylenedioxy)-3,4-diphenyl-6-trichloromethyl-2,5,7,1-trioxaphosphabicyclo[2.2.1^{1,4}]heptane; spatial structure of the product has been elucidated with X-ray diffraction analysis.

Keywords: dioxaphospholane, caged phosphorane, chloral, cascade reaction, 1-hydroxyphosphonate

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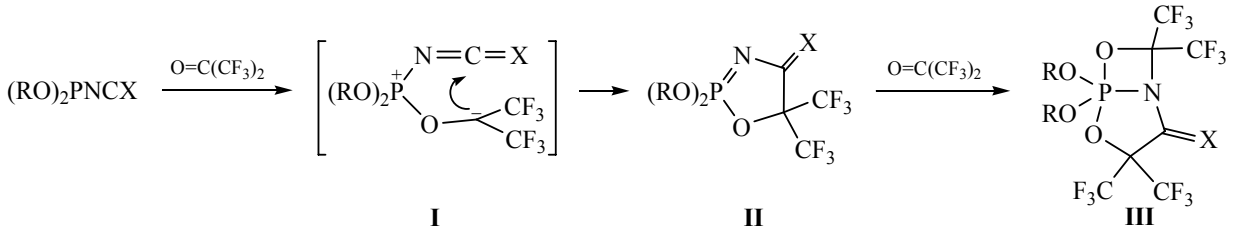
Phosphoranes, a class of pentacoordinate phosphorus compounds, are among key intermediates of nucleophilic substitution reactions at the tetrahedral phosphorus atom [1–3] playing important role in various living cell biochemical processes [4, 5]. Therefore, much attention has been paid to synthesis and study of reactivity of phosphoranes [6, 7]. Caged phosphoranes with the pentacoordinate phosphorus atom being a part of several fused cyclic fragments are of special interest: they possess sufficient rigidity that in certain cases allows preparation of compounds with chiral phosphorus atom [8–10].

One of the first methods to prepare bicyclic caged phosphoranes is apparently the reaction of some P(III) derivatives (such as isocyanatophosphites, isothiocyanatophosphites, and vinylphosphines) with hexafluoroacetone [11]. During the reaction, the unsaturated group linked to the P(III) atom is involved into the stage of generation of bipolar ion with negative charge at the carbon atom (Scheme 1). For instance, the bipolar ion **I** generated from isothiocyanatophosphite and hexafluoroacetone is converted into phospholine **II**. Another hexafluoroacetone molecule being added to the P=N bond of compound **II** yields the bicyclic caged phosphorane **III**. Similarly, reaction of vinyldiphenylphosphine with hexafluoroacetone gives the intermediate oxaphospholene of the ylide structure **IV** further involved in the [2+2] cycloaddition to form dioxaphosphabicycloheptane **V**. Compound **V** may be considered an intermediate of the Wittig reaction; its heating yielded alkene **VI** containing phosphinate group (Scheme 2).

Reaction of salicylic aldehyde with isocyanatophosphites has afforded bicyclic caged phosphoranes **VII** as products of intramolecular addition of hydroxyl group at the P=N bond of the phospholine intermediate (Scheme 3) [12, 13].

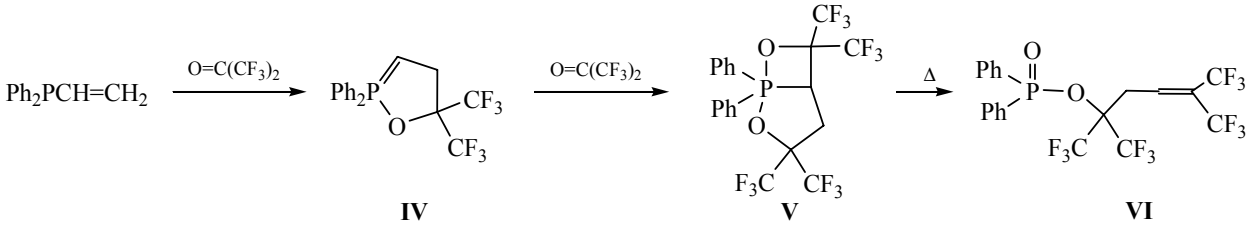
Reaction of isocyanatophosphites with completely enolized hexafluoroacetone proceeds similarly to form caged phosphoranes containing P–C bond **VIII** (Scheme 4) [14–16]. Reaction of 2-(trifluoroacetyl)-phenol with isocyanatophosphites also leads to formation of bicyclic phosphoranes with P–C bond **IX**; at room temperature, pseudorotation has not been observed in these structures, and the P–C bond in tricyclic derivatives occupied axial position of the

Scheme 1.



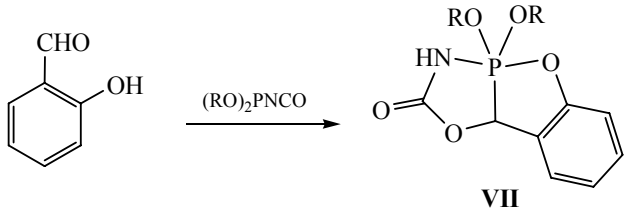
I **II** **III**

Scheme 2.



IV **V** **VI**

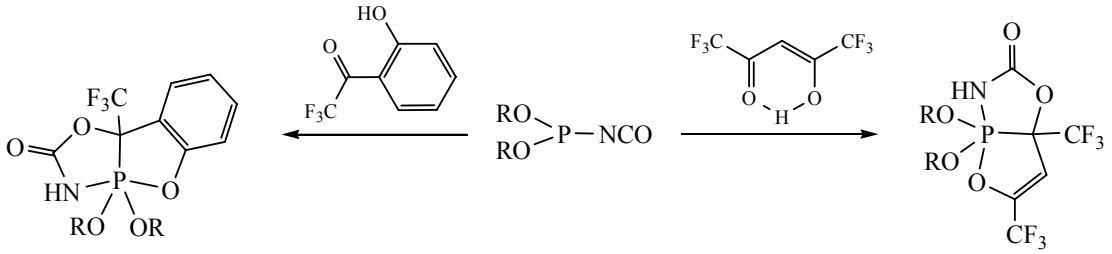
Scheme 3.



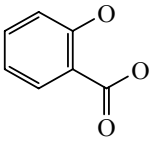
VII

R = Et, $ClCH_2CH_2$.

Scheme 4.



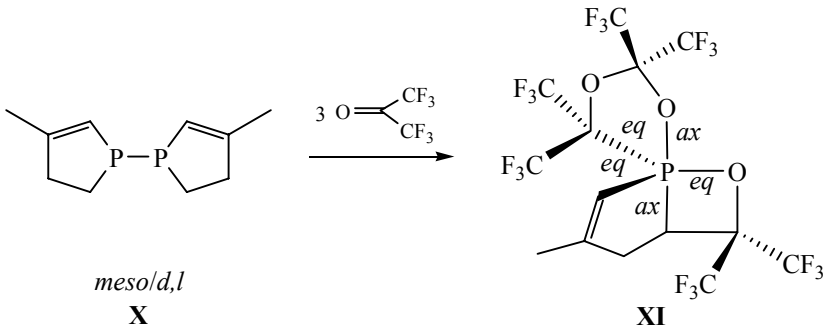
IX **VIII**

IX, R = Me, Et; $(RO)_2$ = $(CH_2O)_2$, $(Me_2CO)_2$; **VIII**, R = Me, Et; $(RO)_2$ = $(Me_2CO)_2$, $(CH_2O)_2$,  .

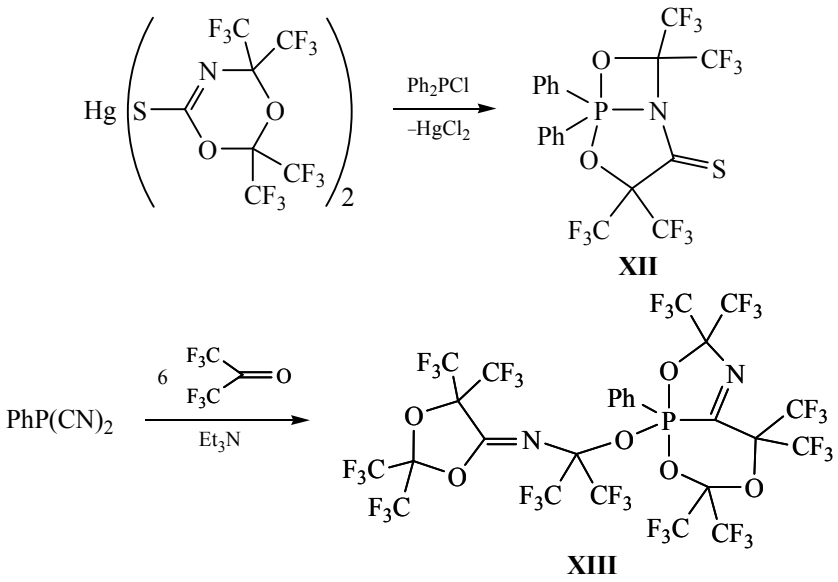
trigonal bipyramid polyhedron of phosphorus atom [17, 18].

The approaches to phosphoranes synthesis under the conditions of kinetic control have allowed isolation of a number of the structures violating the apicophilicity rule. For example, reaction of diastereomeric 1,1-bis(trimethylphospholene-2) **X** with hexafluoroacetone has afforded tricyclic 1,2-oxaphosphetane **XI**, containing the P–C bond in the axial position of distorted trigonal bipyramid of P atom and the fused four- and five-membered cycles [19] (Scheme 5).

Scheme 5.



Scheme 6.



The unusual caged phosphoranes have been prepared via reaction of mercury di[2,2,4,4-tetrakis-(trifluoromethyl)-4*H*-1,3,5-dioxazine-6-thiolate] with diphenylchlorophosphine (**XII**) and of phenyldicyanophosphine with hexafluoroacetone in the presence of triethylamine (**XIII**) (Scheme 6); the products structures have been elucidated by X-ray diffraction analysis [20].

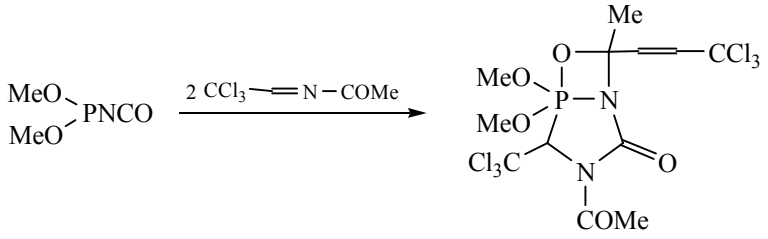
Dimethyl isocyanatophosphite also reacts with activated imines via the both reactive sites to yield bicyclic derivative **XIV** via the intermediate formation of phospholine [21].

The P(III) derivatives containing alkyl substituent at the phosphorus atom have been recognized as another class of parent compounds to prepare caged phosphoranes. For example, (4-bromophenyl)ethynylphosphetane **XV** has reacted with hexafluoroacetone in the 1 : 2 ratio to give bicyclic phosphorane **XVI** (Scheme 8); the product molecule is a distorted trigonal bipyramid (OPO angle 159.7°) with pentamethylphosphetane ring as its base [22].

Reaction of dialkyl alkynylphosphonites with carbonyl compounds activated by electron-acceptor substituents also proceeds at the reagents ratio of 1 : 2 yielding bicyclic phosphoranes **XVII** (Scheme 9); the structures of some of the products have been confirmed by X-ray diffraction [23–30]. Reaction of *O*,*O*-dimethyl (phenylethynyl)phosphonite with *N*,*N*-diphenylcarbodiimide proceeds similarly with formation of caged phosphorane **XVIII** [31] (Scheme 9).

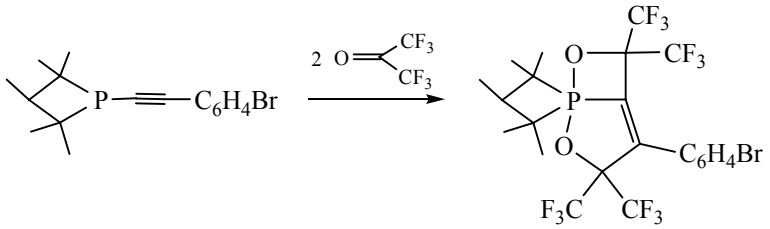
Structures of dioxaphosphabicyclononanes **XIX**–**XXI** (Scheme 10) have been studied by NMR spec-

Scheme 7.



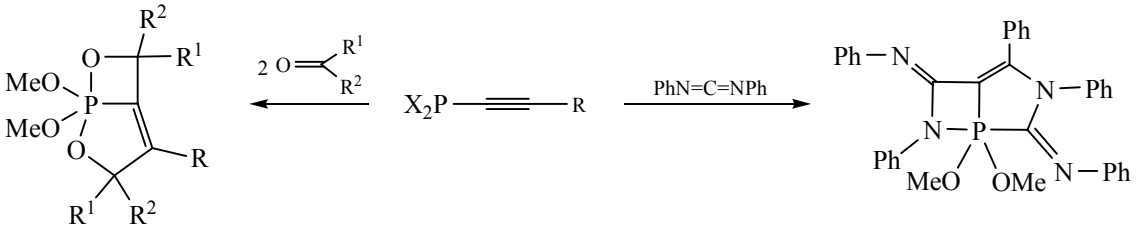
XIV

Scheme 8.



XV **XVI**

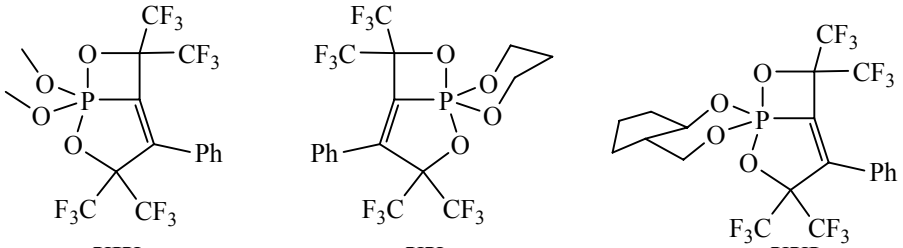
Scheme 9.



XVII **XVIII**

X_2 = $(OMe)_2$, $(OEt)_2$, $(OCH_2)_2CH_2$, $(OCH_2)_2CMe_2$; R^1, R^2 = CF_3, CF_3; CF_3, COOEt; Me, COOEt; Ph, COOEt; COOEt, COOEt; R = Ph, *t*-Bu.

Scheme 10.



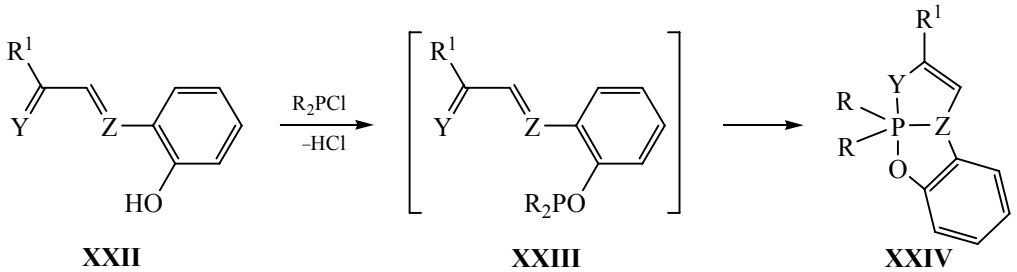
XIX **XX** **XXI**

troscopy and X-ray diffraction analysis; the oxygen atoms of the bicyclic system occupy apical positions of noticeably distorted trigonal bipyramid [28–30, 32].

Reactions of chlorophosphines with imines **XXII** prepared from *ortho*-aminophenol, cinnamic aldehyde or its derivatives as well as dibenzoyl proceeds via intermediate formation of P(III) compounds **XXIII**. The latter undergo intramolecular [1+4] cycloaddition yielding caged phosphoranes **XXIV** (Scheme 11); the products structure has been confirmed by X-ray diffraction analysis [33–36].

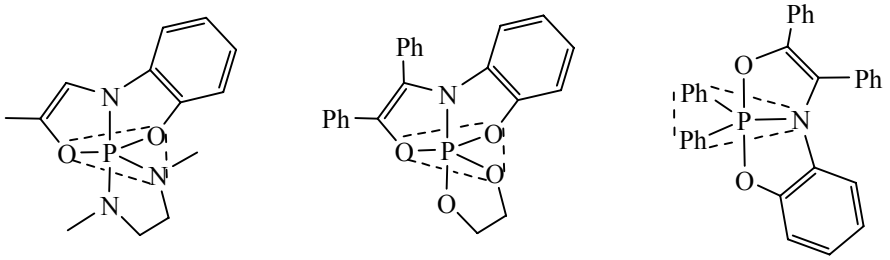
Phosphorylation of *ortho*-hydroxyarylcarbonyl compounds with phenyldichlorophosphine has afforded phosphoranes **XXVI** in high yield as products of

Scheme 11.



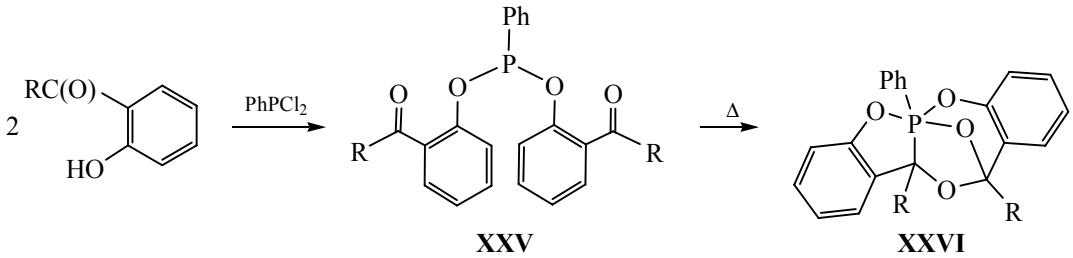
XXII **XXIII** **XXIV**

Y, Z = O, N; O, CH; CHPh, N; R^1 = H, Me; R = Me, Ph, OMe; R_2 = $(CH_2)_2$, $MeN(CH_2)_2NMe$, $C_6H_4O_2$-1,2.



XXIVa **XXIVb** **XXIVc**

Scheme 12.



XXV **XXVI**

R = H, Me, CF_3, Ph, Me_5C_6, OMe.

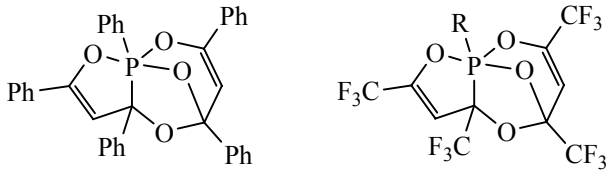
cyclization of P(III) derivatives **XXV** (Scheme 12); compounds **XXVI** contain several chiral centers [37]. Similar caged phosphorane **XXVI** (R = Me) has been prepared via acidolysis of (2-acetylphenoxy)phenyl-*N*,*N*-diethylaminophosphonite with acetic acid [38].

Reactions of phenyldichlorophosphine with dibenzoylmethane, 2-trifluoroacetylphenol, trifluoro-, or hexafluoroacetylacetone also proceed via initial formation of P(III) derivatives followed by their cyclization in phosphoranes **XXVII** and **XXVIII** (Scheme 13) [39–42].

Recently, we have developed a new method to prepare caged compounds of pentacoordinate phosphorus based on cascade reactions of compounds containing activated multiple bonds with P(III) derivatives containing carbonyl or imine group in γ- or δ-position with respect to the phosphorus atom (Scheme 14). This method has allowed preparation of phosphoranes **XXIX**–**XXXII** with high regio- and stereoselectivity [43–45].

In the present work we report on further development of the method using 4,5-dimethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane **XXXIII**, a such P(III) derivative containing several chiral centers. The compound was prepared via phosphorylation of benzoin in the presence of triethylamine with 4,5-dimethyl-2-chloro-1,3,2-dioxaphospholane, the latter formed from *meso*-form of 2,3-butanediol. According to the $^{31}P–\{^1H\}$ NMR data, phospholane **XXXIII** was formed as a mixture of two diastereomers in the ratio of ≈ 5 : 1. Its reaction with chloral containing prochiral carbonyl group proceeded under mild conditions (20°C,

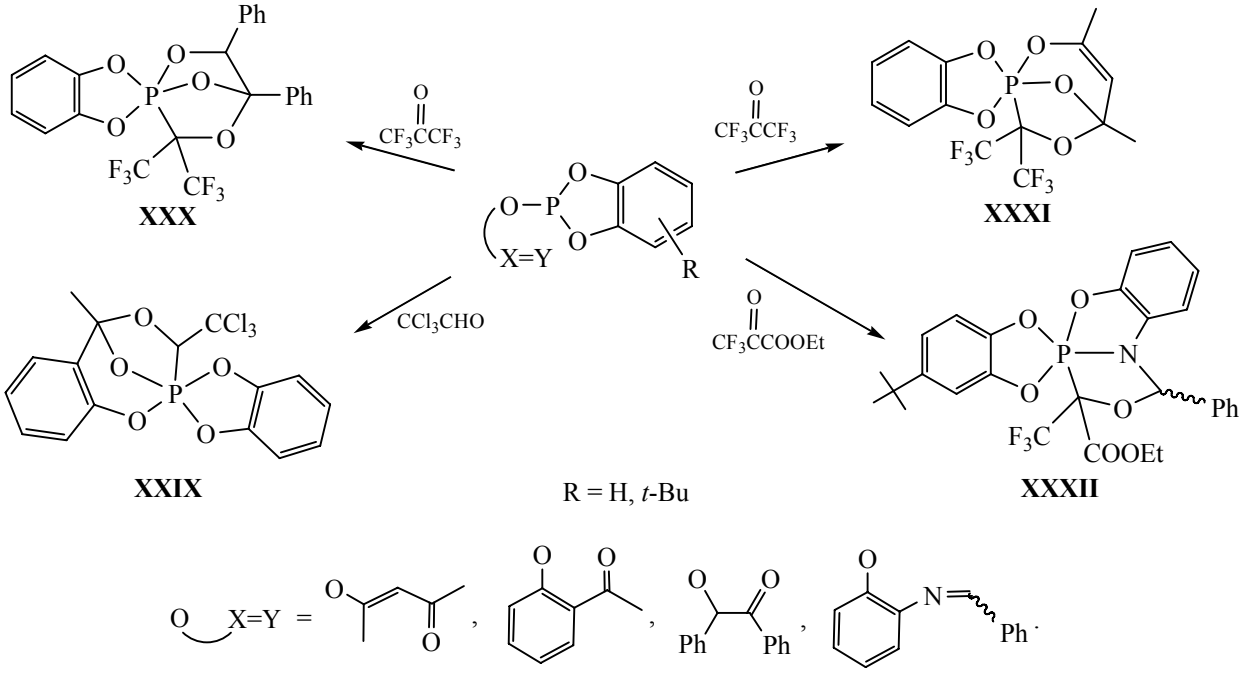
Scheme 13.



XXVII **XXVIII**

R = Me, Et, *i*-Pr, Ph, CH_2Ph, Me_3SiCH_2.

Scheme 14.



XXX **XXXI** **XXIX** **XXXII**

R = H, *t*-Bu

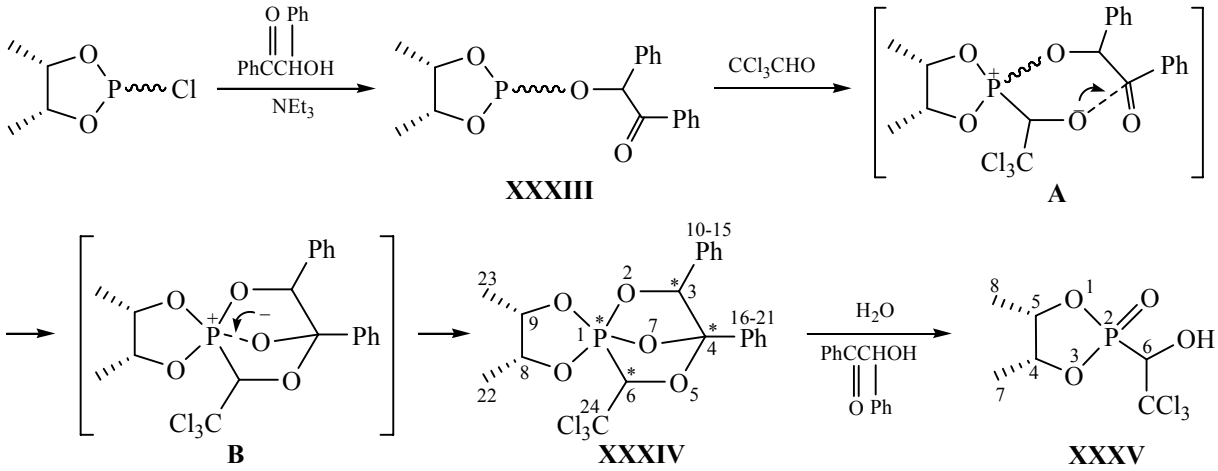
CH_2Cl_2) to form the caged phosphorane, 1,1-(2,2-dimethylethylenedioxy)-3,4-diphenyl-6-trichloromethyl-2,5,7,1-trioxaphosphabicyclo[2.2.1^{1,4}]heptane **XXXIV** with almost quantitative yield, high regioselectivity, and moderate stereoselectivity (Scheme 15).

$^{31}P–\{^1H\}$ NMR spectrum of **XXXIV** contained the upfield-shifted signals at δ_P –18.0, –18.2, and –18.3 ppm (d_1, d_2, d_3 in a ratio of 3 : 1 : 1), typical of pentacoordinate phosphorus surrounded by four P–O bonds and one P–C bond, as part of bicyclic scaffold. Basing on the NMR spectroscopy data ($^{13}C–\{^1H\}$ and ^{13}C), we proposed the caged structure of the prepared compound, confirmed by multiplicity of the C^3, C^4, and C^6 signals (doublets turning into multiplets during recording the ^{13}C NMR spectrum).

The reaction apparently started with nucleophilic attack of the phosphorus atom at the carbon atom of chloral and gave bipolar ion **A**; further intramolecular attack of the alkoxide anion at the exocyclic carbonyl group yielded bipolar ion **B**. The latter was converted into the final product **XXXIV** via attack of the oxygen at the phosphorus atom.

The structure of phosphorane **XXXIV** was determined with X-ray diffraction analysis using monocrystal of one of the isolated diastereomers (from CH_2Cl_2). The molecule geometry is presented in Fig. 1; selected geometry parameters are listed in Table. Configuration of the chiral atoms was of $C^3_RC^4_SC^6_SC^8_SP^1_R/C^3_SC^4_RC^6_RC^8_RP^1_S$; as deviation of the phosphorus atom off the $O^2–O^9–C^6$ plane was fairly small [by 0.096(1) Å], geometry of the phosphorus atom in compound **XXXIV** was a slightly distorted trigonal bipyramid with P^1, O^2, O^9, and C^6 atoms being located in its base plane within 0.072(1) Å. The O^7 and O^8

Scheme 15.



atoms located in apical positions deviated from the plane by 1.696(3) and –1.649(3) Å [the $O^7P^1O^8$ bond angle of 174.9(2)°]. The other bond angles ($O^8P^1C^9$, $O^8P^1C^6$, $O^2P^1O^8$, $O^7P^1C^6$, $O^7P^1O^2$, and $O^7P^1O^9$) ranged from 85.1(2) to 94.5(2)°, the sum of the valence angles $O^2P^1C^6$, $O^9P^1C^6$, and $O^2P^1O^9$ in the base being of 358.9(2)°; that additionally confirmed that the phosphorus coordination polyhedron was an almost regular trigonal bipyramid. The equatorial bonds P^1–O^2 and P^1–O^9 were somewhat shorter [1.608(4) and 1.593(4) Å], than the axial bonds P^1–O^7 and P^1–O^8 [1.724(3) and 1.625(3) Å]. Insignificant distortion of the trigonal bipyramid configuration was also confirmed by slight discrepancy of the sums of axial bonds P^1–O^7 and P^1–O^8 lengths [3.349(3) Å] with the $O^7\cdots O^8$ distance [3.345(5) Å]. The equatorial bond P^1–C^6 was 1.858(5) Å long. Five-membered dioxaphospholene ring occupied an axial-equatorial position in the trigonal bipyramid (O^8 being axial and O^9 being equatorial); the ring took the *envelope* conformation with O^8, P^1, O^9, and C^9 atoms being located in the same plane within 0.001(5) Å, and the C^8 atom deviating from that plane by –0.438(5) Å. The atoms C^{22} and C^{23} occupied the axial positions in the ring and deviated from its by –1.940(5) and –0.879 Å; the atoms O^2 and C^6 occupied the axial positions as well and were located at the opposite sides with respect to the $O^8P^1O^9C^9$ plane. The atom O^7 was found almost in the $O^8P^1O^9C^9$ plane [the deviation of 0.142(3) Å]. Conformation of the $P^1C^6O^5C^4O^7$ five-membered ring was of distorted *envelope* (Fig. 2) with phenyl substituent and chloromethyl group as well as the O^2 and O^5 atoms occupying the axial positions. Another five-membered ring of the rigid bicycloheptane system ($P^1O^2C^3C^4O^7$) also took the *envelope* conformation [four-atomic fragment $P^1O^2C^3C^4$ being flat within 0.184(3) Å, and the O^7 atom deviating by –0.843(3) Å]. The substituents in the (O^5, O^9, C^6, O^8, C^{10}) ring were deviated from the plane by 1.231(3), –1.131(3), 1.535(5), 0.993(3), and –1.231(6) Å, respectively.

The phosphorane **XXXIV** eliminated the benzoin fragment when incubated in air, converting into the cyclic phosphonate **XXXV** with high stereoselectivity; the spectral characteristics of the product coincided with those reported elsewhere [46].

In summary, the cascade reaction of 4,5-dimethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane (prepared from the *meso*-form of 2,3-butanediol) with chloral yielded the caged phosphorane containing a P–C bond: 1,1-(1,2-dimethylethylenedioxy)-3,4-diphenyl-6-trichloromethyl-2,5,7,1-trioxaphosphabicyclo-[2.2.$1^{1,4}$]heptane with moderate stereoselectivity.

EXPERIMENTAL

^1H, ^{13}C, ^{13}C–{^1H}, and ^{31}P–{^1H} NMR spectra of the solutions in $CDCl_3$ were registered with Bruker-400 and Bruker-600 (^{13}C) instruments relative to the residual signals of the solvent. IR spectra were recorded using a Bruker Vector-22 spectrometer (KBr pellets). Mass spectra were recorded with a DFS Thermo Electron Corporation instrument (USA); energy of ionizing electrons 70 eV, temperature of the ions source 290°C, the direct injection evaporator heated from 100 to 350°C). The mass spectra were processed taking advantage of Xcalibur software.

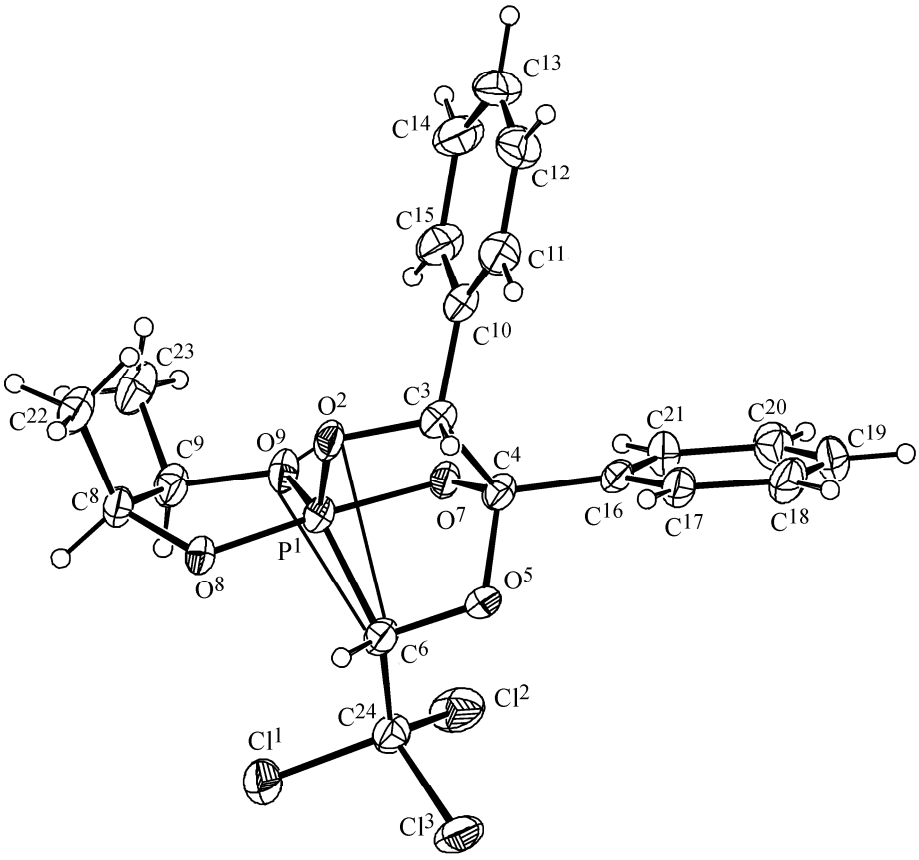


Fig. 1. Geometry of the phosphorane **XXXIV** molecule in the crystal (heat ellipsoids are given with 30% probability; the trigonal bipyramid base is shown with thin lines).

4,5-Dimethyl-2-(2-oxo-1,2-diphenylethoxy)-1,3,2-dioxaphospholane (XXXIII). 4,5-Dimethyl-2-chloro-1,3,2-dioxaphospholane prepared from the *meso*-form of 2,3-butanediol (4.57 g, 0.03 mol) was dropwise added to a mixture of 5.36 g (0.03 mol) of benzoin and 4.17 mL (0.031 mol) of triethylamine in 200 mL of diethyl ether at –5°C under inert atmosphere upon stirring. The reaction mixture was stirred during 2 h being simultaneously self-heated to ambient. The precipitated triethylammonium chloride was filtered off; the filtrate was evaporated in vacuum (10 mmHg). The residue was transparent viscous liquid; it was used further without additional purification. Yield 8.22 g (87%). $^{31}P–\{^{1}H\}$ NMR spectrum (CH_2Cl_2), δ_P, ppm: 146.4, 133.8. Found, %: C 64.81; H 5.31; P 9.77. $C_{18}H_{19}O_4P$. Calculated, %: C 64.76; H 5.76; P 9.39.

1,1-(1,2-Dimethylethylenedioxy)-3,4-diphenyl-6-trichloromethyl-2,5,7,1-trioxaphosphabicyclo[2.2.1^{1,4}]-heptane (XXXIV). A mixture of compound **XXXIII** (6.0 g, 0.02 mol) and chloral (2.68 g, 0.02 mol) in 6 mL of CH_2Cl_2 was incubated under argon during one week at 20°C. Then the reaction mixture was

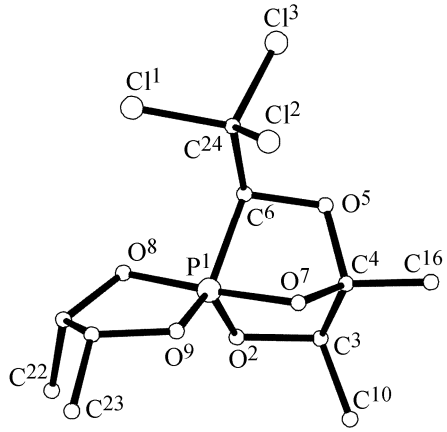


Fig. 2. Rings conformation of trioxaphosphabicycloheptane scaffold of **XXXIV** molecule in the crystal (hydrogen atoms are omitted for clarity).

The selected bond lengths (*d*, Å), bond (φ, deg) and torsion (τ, deg) angles in the molecule of compound **XXXIV**

Bond	*d*	Bond	*d*	Bond	*d*
P^1–O^2	1.608(4)	O^5–C^4	1.479(6)	C^3–C^{10}	1.499(8)
P^1–O^7	1.724(3)	O^5–C^6	1.428(6)	C^4–C^{16}	1.504(7)
P^1–O^8	1.625(3)	O^7–C^4	1.356(6)	C^6–C^{24}	1.517(8)
P^1–O^9	1.593(4)	O^8–C^8	1.437(6)	C^8–C^9	1.513(8)
P^1–C^6	1.858(5)	O^9–C^9	1.474(6)	C^8–C^{22}	1.530(7)
O^2–C^3	1.455(6)	C^3–C^4	1.572(7)	C^9–C^{23}	1.508(7)
Bond angle	φ	Bond angle	φ	Bond angle	φ
$O^2P^1O^7$	90.6(2)	$O^7P^1C^6$	85.6(2)	$C^4C^3C^{10}$	117.0(4)
$O^8C^8C^{22}$	108.8(4)	$O^8P^1O^9$	92.9(2)	$O^5C^4O^7$	106.2(4)
$O^2P^1O^8$	94.5(2)	$O^8P^1C^6$	92.8(2)	$O^5C^4C^3$	107.2(4)
$C^9C^8C^{22}$	116.4(4)	$O^9P^1C^6$	136.6(2)	$O^5C^4C^{16}$	106.3(4)
$O^2P^1O^9$	123.0(2)	$P^1O^2C^3$	113.1(3)	$O^7C^4C^3$	103.5(4)
$O^9C^9C^8$	104.8(4)	$C^4O^5C^6$	109.2(3)	$O^7C^4C^{16}$	116.0(5)
$O^2P^1C^6$	99.3(2)	$P^1O^7C^4$	101.5(3)	$C^3C^4C^{16}$	116.9(5)
$O^9C^9C^{23}$	107.0(4)	$P^1O^8C^8$	114.4(3)	$P^1C^6O^5$	103.7(3)
$O^7P^1O^8$	174.9(2)	$P^1O^9C^9$	115.2(3)	$P^1C^6C^{24}$	120.4(4)
$C^8C^9C^{23}$	117.1(4)	$O^2C^3C^4$	101.3(4)	$O^5C^6C^{24}$	109.9(4)
$O^7P^1O^9$	85.1(2)	$O^2C^3C^{10}$	111.0(4)	$O^8C^8C^9$	103.7(4)
Torsion angle	τ	Torsion angle	τ	Torsion angle	τ
$O^7P^1O^2C^3$	–22.1(3)	$O^7P^1O^9C^9$	175.2(3)	$O^2C^3C^4C^{16}$	168.8(4)
$O^8P^1O^2C^3$	157.0(3)	$O^2P^1C^6O^5$	–56.6(3)	$C^{10}C^3C^4C^{16}$	48.1(6)
$O^9P^1O^2C^3$	–106.6(3)	$O^2P^1C^6C^{24}$	–179.9(4)	$O^2C^3C^4O^5$	–72.1(4)
$C^6P^1O^2C^3$	63.5(3)	$O^7P^1C^6O^5$	33.3(3)	$O^2C^3C4O^7$	39.9(5)
$O^2P^1O^7C^4$	47.0(3)	$P^1O^2C^3C^4$	–5.4(4)	$O^5C^4C^{16}C^{17}$	116.4(5)
$O^9P^1O^7C^4$	170.1(3)	$C^4O^5C^6P^1$	–7.3(4)	$C^3C^4C^{16}C^{17}$	–124.0(6)
$C^6P^1O^7C^4$	–52.3(3)	$C^4O^5C^6C^{24}$	122.6(4)	$C^3C^4C^{16}C^{21}$	57.7(7)
$O^9P^1O^8C^8$	–19.4(4)	$P^1O^7C^4C^3$	–55.4(4)	$O^8C^8C^9O^9$	–28.2(5)
$C^6P^1O^8C^8$	–156.4(4)	$P^1O^7C^4C^{16}$	175.2(4)	$O^8C^8C^9C^{23}$	–146.6(4)
$O^2P^1O^9C^9$	–97.4(3)	$P^1O^9C^9C^{23}$	142.5(4)	$C^{22}C^8C^9O^9$	91.1(5)

evaporated in vacuum (12 mmHg) to about half of the mass; white solid product precipitated. Yield 7.6 g (80%), mp 171–173°C (CH_2Cl_2). IR spectrum, ν, cm^{-1}: 3446 w, 3232 w, 3067 w, 3034 w, 2987, 2939, 2661, 2252, 1681, 1598, 1581, 1496, 1450, 1386, 1338, 1304, 1266, 1178, 1082, 1018, 1002, 964, 909, 837, 821, 738, 698, 649, 624, 595. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) (d_1, d_2), δ, ppm: 8.00 br.d (H^{17}, $^3J_{HH}$ 7.9 Hz), 7.49 br.d (H^{11}, $^3J_{HH}$ 7.9 Hz), 7.68 br.d.d (H^{18}, $^3J_{HH}$ 7.3, $^3J_{HH}$ 7.8 Hz), 7.54 br.d.d ($^3J_{HH}$ 7.4, $^3J_{HH}$

7.9 Hz), 7.42 br.d.d ($^3J_{HH}$ 7.9, $^3J_{HH}$ 7.3 Hz), 7.35 br.m ($H^{12,13,19}$), 5.98 s (H^3), 4.56 d (H^6, $^2J_{PH}$ 11.7 Hz), 4.59 d (H^6, $^2J_{PH}$ 12.0 Hz), 4.81 m and 3.69 m ($H^{8,9}$), 1.22 d and 1.33 d ($H^{22,23}$, $^3J_{HH}$ 6.4, $^3J_{HH}$ 6.4 Hz), 1.22 d ($H^{22,23}$, $^3J_{HH}$ 8.9 Hz). ^{1}H NMR spectrum (600 MHz, $CDCl_3$) (d_1, d_2, d_3), δ, ppm: 7.94 m ($H^{11,17}$), 7.55 d.d.t ($H^{13,19}$, $^3J_{HH}$ 7.7, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.2 Hz), 7.42 m ($H^{12,18}$), 7.35–7.36 m ($H^{11,17}$), 5.98 s (H^3), 4.86 m, 4.81 m, 4.74 m and 3.96 m ($H^{8,9}$), 4.70 d (H^6, $^2J_{PH}$ 11.0 Hz), 4.56 d (H^6, $^2J_{PH}$ 11.9 Hz), 4.55 d (H^6, $^2J_{PH}$ 11.6 Hz), 1.22 d ($H^{18,19}$, $^3J_{HH}$ 6.4 Hz), 1.23 d ($H^{18,19}$, $^3J_{HH}$ 6.4 Hz), 1.34 d ($H^{18,19}$, $^3J_{HH}$ 6.4 Hz), 1.38 d ($H^{22,23}$, $^3J_{HH}$ 6.2 Hz), 1.46 d ($H^{22,23}$, $^3J_{HH}$ 6.3 Hz), 1.47 d ($H^{22,23}$, $^3J_{HH}$ 6.3 Hz). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (the data given in parentheses are for the ^{13}C–{1H} spectra): 87.46 br.d.d (d) (C^3, $^1J_{HC3}$ 153.2–156.2, $^2J_{PC3}$ 40.7 Hz) (d_1), 88.08 br.d.d (d) (C^3, $^1J_{HC3}$ 153.2–156.2, $^2J_{PC3}$ 30.5 Hz) (d_2), 98.27 br.d (d) (C^4, $^2J_{PC4}$ 25.4 Hz) (d_1), 98.48 br.d (d) (C^4, $^2J_{PC4}$ 27.0 Hz) (d_2), 99.35 br.d (d) (C^4, $^2J_{PC4}$ 28.0 Hz) (d_3), 83.35 d.d (d) (C^6, $^1J_{HC6}$ 161.0, $^1J_{PC6}$ 161.2 Hz) (d_1), 83.75 d.d (d) (C^6, $^1J_{PC6}$ 161.7, $^1J_{HC6}$ 161.0 Hz) (d_2), 82.96 d.d (d) (C^6, $^1J_{PC6}$ 160.8, $^1J_{HC6}$ 160.5 Hz) (d_3), 72.91 br.d (d) ($C^{8,9}$, $^1J_{HC}$ 152.6, $^2J_{PC}$ 2.5–2.8 Hz) (d_1, d_2), 72.81 br.d (br.d) ($C^{8,9}$, $^1J_{HC}$ 152.0 Hz) (d_1, d_2), 70.42 br.d (d) ($C^{8,9}$, $^1J_{HC}$ 150.8, $^2J_{PC}$ 9.2 Hz) (d_1, d_2), 70.02 br.d (d) ($C^{8,9}$, $^1J_{HC}$ 146.6, $^2J_{PC}$ 5.6 Hz) (d_1, d_2), 135.77 br.m (br.s) (C^{10}), 138.88 br.d.t (br.d) (C^{16}, $^2J_{PC16}$ 8.7, $^3J_{HC16}$ 6.0–7.0 Hz), 133.77 d.t (s) (C^{19}, $^1J_{HC19}$ 162.8, $^3J_{HC19}$ 7.3–7.4 Hz), 125.68 d.m (s), 126.41 d.m (s), 126.47 d.m (s), 126.91 d.m (s), 127.55 d.m (s), 127.64 d.m (s), 127.71 d.m (s), 127.95 d.m (s), 128.23 d.m (s), 128.58 d.m (s), 128.97 d.m (s), 128.99 d.m (s), 129.05 d.m (s) ($C^{11–13}$, $C^{17–19}$, accurate assignment of the signals was complicated due to isomerism and non-equivalence of the carbon atoms), 15.78 br.q.d (d) ($C^{22,23}$, $^1J_{HC}$ 128.6, $^3J_{PC}$ 11.4–12.0 Hz), 15.40 br.q.m (br.s) ($C^{22,23}$, $^1J_{HC}$ 127.4 Hz). ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2), δ_P, ppm: –18.0 (s), –18.2 (s), –18.3 (s) (d_1, d_2, d_3 in a ratio of 3 : 1 : 1). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 476.01 (100.0) $[M]^{+\cdot}$ (calculated for $C_{20}H_{20}Cl^{35}{}_3O_5P$: 476), 478.01 (95.9), 480.01 (31.6), 477.01 (21.6), 479.01 (21.1), 481.01 (6.8), 478.02 (3.3), 482.00 (3.3), 480.02 (2.3), 482.01 (1.0). Found, %: C 50.47; H 4.39; P 6.26. $C_{20}H_{20}Cl_3O_5P$. Calculated, %: C 50.31; H 4.19; P 6.49.

2-(1-Hydroxy-2,2,2-trichloroethyl)-4,5-dimethyl-2-oxo-1,3,2-dioxaphospholane (XXXV). A solution of compound **XXXIV** in CH_2Cl_2 was incubated without protection against air moisture. Three days later formation of precipitate was observed; it was filtered off and dried in vacuum (10 mmHg). mp 171°C. IR spectrum, ν, cm^{-1}: 3424, 3194, 2999, 2969, 2907, 2853, 1626, 1422, 1386, 1314, 1258, 1218, 1165, 1097, 1073, 1019, 922, 956, 899, 860, 836, 819, 786, 769, 729, 662, 610, 574, 513, 493, 461, 432. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 7.94 d.d (OH, $^3J_{PH}$ 13.4, $^3J_{HH}$ 8.1 Hz), 4.83 d.d [$H^{4,5}$, B-part of ABX-system, $^3J(PH_B)$ 10.5, $^3J(H_AH_B)$ 8.1 Hz], 4.76 d.d [$H^{4,5}$, A-part of ABX-system, $^3J(PH_A)$ 13.0, $^3J(H_BH_A)$ 8.1 Hz], 4.76 d.d (H^6, $^2J_{PH}$ 11.4, $^3J_{HH}$ 8.1 Hz), 1.30 s (H^7), 1.28 s (H^8). ^{31}P–{^{1}H} NMR spectrum (36.5 MHz, DMSO-d_6): δ_P 30.1 ppm. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 282 (11.2) $[M]^{+\cdot}$ (calculated for $C_6H_{10}Cl^{35}{}_3O_4P$: 282), 247 $[M - Cl]^+$, 211 $[M - 2Cl - H]^+$, 165 $[M - CCl_3]^+$, 135 $[M - CH(OH)CCl_3]^+$, 56 $[C_4H_8]^+$.

Single crystal X-ray diffraction of **XXXIV** was performed using a Bruker Smart APEX II CCD automated diffractometer (graphite monochromator, MoK_α irradiation, λ 0.71073 Å, ω-scanning, 293 K). Semi-empirical correction for absorption was performed using SADABS software [47]. The structure was solved by the direct method using SIR software [48] and refined first in isotropic and then in anisotropic approximation using SHELXL-97 routine [49] of WinGX software package [50]. Hydrogen atoms H^{8A} and H^{8B} were revealed from the difference Fourier series and refined isotropically. Other hydrogen atoms were placed at the geometrically calculated positions and involved into refinement with a *rider* model. Data collection and processing as well as the unit cell parameters refinement were performed using APEX2 software [51]. Analysis of the intramolecular interactions and the figures were performed with PLATON [52] and ORTEP software [53].

The crystals of compound **XXXIV** were colorless, prismatic, triclinic, $C_{20}H_{20}Cl_3O_5P$, M_{calc} 477.68; parameters of the unit cell: *a* 6.200(4), *b* 9.413(6), *c* 18.75(1) Å, α 94.687(7), β 98.121(7), γ 103.277(7)°, *V* 1047(1) $Å^3$, d_{calc} 1.52 g/cm^3, *Z* 2, space group *P*-1, μ(MoK_α) 5.44 cm^{-1}. Scanning angle range $2.2° < \theta < 28.0°$; 4883 independent reflections were measured, 1396 showing $I \geq 2\sigma$. Final values of divergence factors were *R* 0.0567 and R_w 0.0957 from 1396 reflections with $F > 2\sigma(F^2)$.

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