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Reaction of 2-Chlorophenylacetylene with 2,2,2-Trichloro-1,3,2λ^5-benzodioxaphosphole

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Abstract—According to the ^{13}C and ^{1}H NMR data (one- and two-dimensional spectra), *o*-chlorophenylacetylene reacts with 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole under mild conditions to give a mixture of diastereoisomeric 2,6-dichloro-4-(2-chlorophenyl)-1,2λ^5-benzoxaphosphinin-2-ones differing in the configuration of the phosphorus atom and rotation of the *o*-chlorophenyl group about the C^4–C_{arom} bond. Hydrolysis of that mixture leads to 6-chloro-4-(2-chlorophenyl)-2-hydroxy-1,2λ^5-benzoxaphosphinin-2-one as a single stereoisomer.

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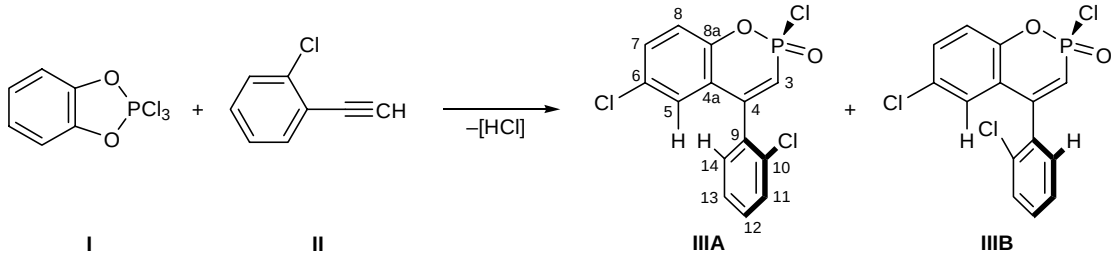
Reactions of phosphorus pentachloride with acetylenes underly a general method for the synthesis of practically important compounds possessing a phosphorus–carbon bond [1–3]. As a rule, these reactions require a double excess of phosphorus pentachloride: electrophilic addition of PCl_5 at the triple bond of an acetylenic substrate gives intermediate phosphoranes which readily react with the second PCl_5 molecule to produce the corresponding phosphonium hexachlorophosphates(V). Replacement of phosphorus pentachloride by 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (**I**) changes the reaction direction so that the products are derivatives of the 1,2λ^5-benzoxaphosphinine heterocyclic system, which can be regarded as phosphorus analogs of naturally occurring coumarin [4–8]. Phosphorus-containing coumarin derivatives attract considerable interest as potential biologically active substances [9].

The goal of the present work was to examine the reaction of dioxaphosphole **I** with 2-chlorophenylacetylene (**II**), the latter containing a substituent in the *ortho* position of the benzene ring. The expected product of this reaction, 2,6-dichloro-4-(2-chlorophenyl)-1,2λ^5-benzoxaphosphinin-2-one (**III**), could exist as different diastereoisomers due to the presence of a chiral phosphorus atom and atropoisomerism resulting from restricted rotation about the carbon–carbon bond between the C^4 atom and *ortho*-substituted benzene ring. We previously noted that some carbon atoms in the phenyl group attached to C^4 of benzophosphinine heteroring give broadened signals in the ^{13}C NMR spectra, which may be due to the lack of free rotation about the C_{arom}–C^4 bond [4–8].

We found that compound **I** readily reacted with substituted acetylene **II** in methylene chloride with liberation of hydrogen chloride. The ^{31}P–{^{1}H} NMR spectrum (121.42 MHz, CH_2Cl_2) of the reaction mixture contained two singlets at δ_P 17.1 and 17.2 with an intensity ratio of 1:1, which were converted into a broadened doublet with a coupling constant $^2J_{PH}$ of

Scheme 1.



I **II** **IIIA** **IIIB**

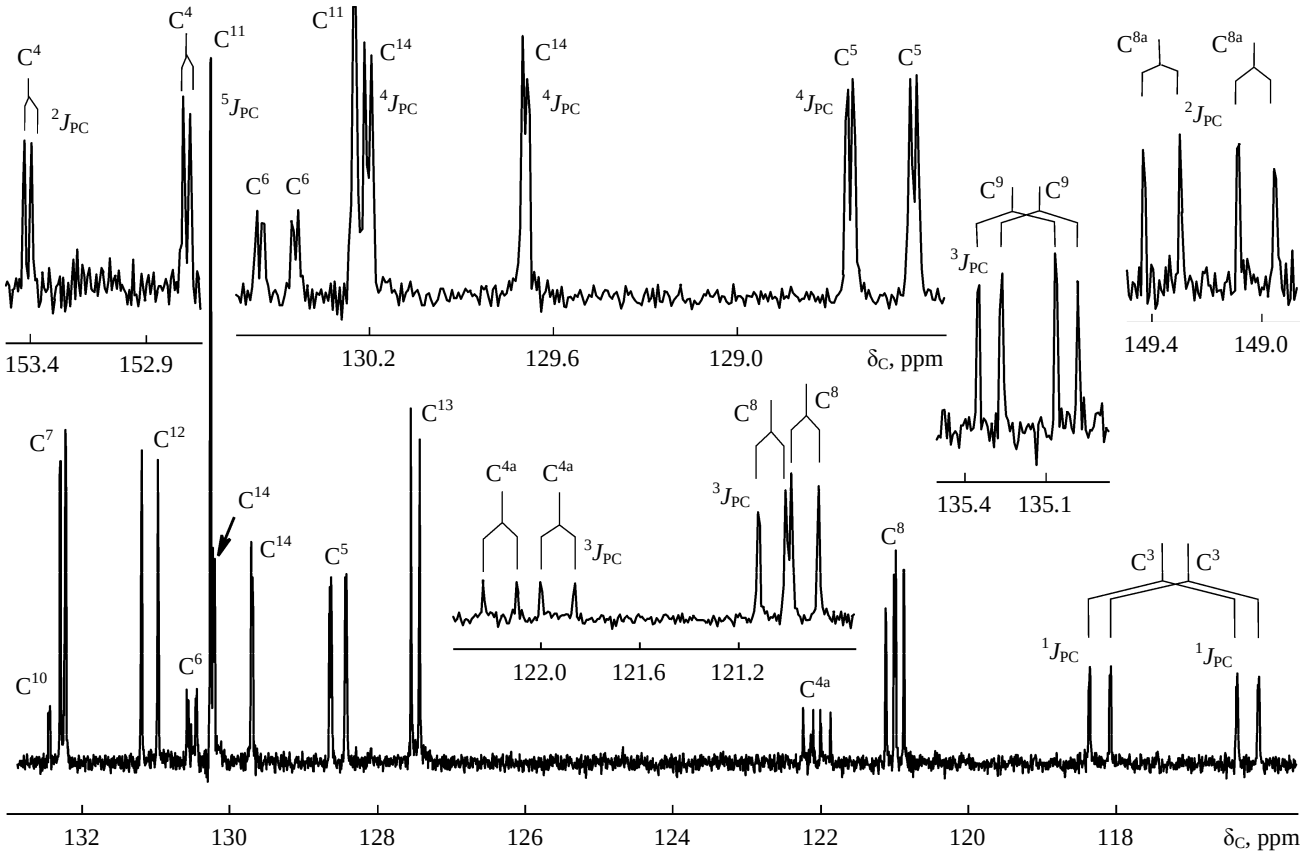
Parameters of the ^{13}C NMR spectra of 1,2λ^5-benzoxaphosphinines **III** (125.47 MHz) and **IV** (125.47 and 150.9 MHz)

Atom	Compound **III** ($CDCl_3$)			Compound **IV** (acetone-d_6)[a]		
	δ, ppm (*J*, Hz)	cross peak		δ, ppm (*J*, Hz)	cross peaks	
		HMBC	HSQC		HMBC	HSQC
C^3	117.02 d ($^1J_{PC}$ = 150.4), 116.75 d ($^1J_{PC}$ = 152.1)	–	3-H	126.14 d ($^1J_{PC}$ = 159.6) [119.64 d ($^1J_{PC}$ = 168.0)] {119.03 d.d (d)[b] ($^1J_{PC}$ = 166.4, $^1J_{HC}$ = 164.9)}	–	3-H
C^4	153.35 d ($^2J_{PC}$ = 2.2), 152.67 d ($^2J_{PC}$ = 2.0)	3-H, 5-H, 14-H	–	144.30 s [150.48 s] {148.66 m (d) ($^2J_{PC}$ = 2.0, $^3J_{5\text{-}H}$ = 4.0, $^3J_{3\text{-}H}$ = 3.7, $^3J_{14\text{-}H}$ = 4.0–4.3)}	3-H, 5-H, 14-H	–
C^{4a}	121.90 d ($^3J_{PC}$ = 17.6), 121.76 d ($^3J_{PC}$ = 17.7)	3-H, 8-H	–	125.56 d ($^3J_{PC}$ = 17.7) [124.58 d ($^3J_{PC}$ = 17.8)] {123.24 d.d.d.d (d) ($^3J_{PC}$ = 16.4, $^3J_{3\text{-}H}$ = 8.9, $^3J_{8\text{-}H}$ = 6.1, $^2J_{5\text{-}H}$ = 1.0)}	3-H, 8-H	–
C^5	128.42 d ($^4J_{PC}$ = 1.4), 128.63 d ($^4J_{PC}$ = 1.3)	7-H	5-H	127.25 s [128.47 s] {127.15 br.d.d (d) ($^1J_{HC}$ = 164.9, $^3J_{HC}$ = 5.9, $^4J_{PC}$ = 1.0)}	7-H	5-H
C^6	130.56 d ($^5J_{PC}$ = 1.3), 130.44 d ($^5J_{PC}$ = 1.2)	5-H, 7-H, 8-H	–	126.54 s [129.31 s] {127.72 d.d.d (d) ($^3J_{HC}$ = 11.4, $^2J_{7\text{-}H}$ = 3.6, $^2J_{5\text{-}H}$ = 3.6)}	5-H, 7-H, 8-H	–
C^7	132.29 s, 132.22 s	5-H	7-H	129.64 s [131.62 s] {130.08 d.d (s) ($^1J_{HC}$ = 169.0, $^3J_{HC}$ = 6.2)}	5-H, 8-H	7-H
C^8	121.06 d ($^3J_{PC}$ = 8.5), 120.98 d ($^3J_{PC}$ = 8.5)	7-H	8-H	121.70 d ($^3J_{PC}$ = 6.0) [122.02 d ($^3J_{PC}$ = 7.2)] {121.45 d.d.d (d) ($^1J_{HC}$ = 163.6, $^3J_{PC}$ = 7.3, $^2J_{HC}$ = 3.1)}	7-H	8-H
C^{8a}	149.36 d ($^2J_{PC}$ = 10.1), 149.02 d ($^2J_{PC}$ = 10.1)	5-H, 7-H, 8-H	–	152.84 d ($^2J_{PC}$ = 7.2) [151.54 d ($^2J_{PC}$ = 7.4)] {150.10 d.d.d.d (d) ($^3J_{HC}$ = 10.7, 8.6, (J_{PC} = 7.4, $^2J_{HC}$ = 3.8)}	5-H, 7-H, 8-H	–
C^9	135.21 d ($^3J_{PC}$ = 21.5), 135.12 d ($^3J_{PC}$ = 21.1)	3-H, 11-H, 13-H	–	139.33 d ($^3J_{PC}$ = 17.0) [138.55 d ($^3J_{PC}$ = 18.3)] {136.84 m (d) ($^3J_{PC}$ = 19.2, $^3J_{3\text{-}H}$ = 6.7, $^3J_{13\text{-}H}$ = 6.1, $^3J_{11\text{-}H}$ = 6.1, $^2J_{HC}$ = 1.5)}	3-H, 11-H, 13-H	–
C^{10}	132.43 br.s, 132.20 br.s	12-H, 14-H	–	133.24 s [133.57 s] {131.90 d.d.d (s) ($^3J_{14\text{-}H}$ = 10.1, $^3J_{12\text{-}H}$ = 10.1, $^2J_{HC}$ = 2.5)}	11-H, 12-H, 14-H	–
C^{11}	130.25 s, 130.25 s	12-H, 13-H	11-H	130.47 s [130.99 s] {131.06 d.d (s) ($^1J_{HC}$ = 165.2, $^3J_{HC}$ = 8.3)}	13-H	11-H
C^{12}	131.19 s, 130.96 s	14-H	12-H	130.75 s [131.68 s] {130.08 d.d.d.d (s) ($^1J_{HC}$ = 167.2, $^3J_{HC}$ = 7.5, $^2J_{11\text{-}H}$ = 1.3, $^2J_{13\text{-}H}$ = 1.3)}	14-H	12-H
C^{13}	127.54 s, 127.42 s	11-H	13-H	128.43 s [128.76 s] {128.17 d.d (s) ($^1J_{HC}$ = 164.8, $^3J_{HC}$ = 7.6)}	11-H	13-H
C^{14}	130.20 d ($^4J_{PC}$ = 1.6), 129.69 d ($^4J_{PC}$ = 1.2)	12-H	14-H	132.01 s [131.85 s] {131.08 ush.d.d (d) ($^1J_{HC}$ = 165.3, $^3J_{HC}$ = 8.3, $^4J_{PC}$ = 1.5)}	12-H	14-H

[a] The spectral parameters obtained from a solution in CD_3OD are given in brackets, and those recorded in DMSO-d_6–acetone-d_6 (1:4) (150.9 MHz) are given in braces.

[b] Hereinafter, the signal multiplicity in the ^{13}C–{^1H}NMR spectrum is given in parentheses.

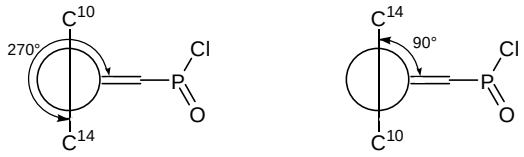
23–34 Hz. In the downfield region of the ^1H NMR spectrum (500 MHz, $CDCl_3$) we observed two well resolved doublets at δ 6.33 ($^2J_{PH}$ = 23.6 Hz) and 6.34 ppm ($^2J_{PH}$ = 23.0 Hz), belonging to the P–CH=C proton. The mass spectrum (electrospray ionization) of the reaction mixture purified from volatile impurities contained a peak with *m*/*z* 343, which corresponds to the molecular ion ($[M - H]^+$) of a $C_{14}H_8{}^{35}Cl_3O_2P$ compound. The above spectral data indicate that the reaction gives two compounds having a benzoxaphosphinine structure in which the benzo fragment is substituted by chlorine. Taking into account our previous results obtained by studying the reaction of phosphole **I** with phenylacetylene [4], we presumed that the prod-



^{13}C NMR spectrum ($CDCl_3$, 125.77 MHz) of a mixture of diastereoisomers **IIIA** and **IIIB**.

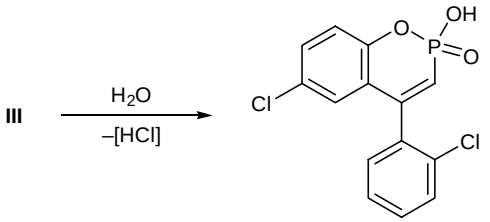
ucts are two diastereoisomeric 1,2λ^5-benzoxaphosphinines **IIIA** and **IIIB** (Scheme 1).

Their structure was finally proved by the ^{13}C–{^1H} and two-dimensional NMR spectra using homo- (COSY ^1H–^1H) and heteronuclear (HETCOR ^1H–^{13}C) correlation techniques optimized for direct (HSQS) and long-range coupling constants (HMBC). The results are given in table. Figure shows fragments of the ^{13}C–{^1H} NMR spectrum (125.47 MHz, $CDCl_3$) of a mixture of diastereoisomers **IIIA** and **IIIB**. It is seen that each carbon nuclei (except for C^{11}) gives two signals corresponding to different diastereoisomers. The maximal nonequivalence is observed for C^3, C^4, C^5, C^{8a}, and C^{14}. Signals from carbon atoms in the 2-chlorophenyl substituents were assigned on the basis of the HMBC spectrum (heteronuclear correlation using $^2J_{HC}$ and $^3J_{HC}$ couplings); on the other hand, satisfactory results were obtained by calculation of chemical shifts according to the additivity scheme using 2,6-dichloro-4-phenyl-1,2λ^5-benzoxaphosphinin-2-one [4] as model structure. Unfortunately, the obtained data were insufficient to assign all signals to particular diastereoisomers **A** and **B**. On the basis of the stereochemical relation between the long-range coupling constant $^4J_{HH}$ in allyl systems (HCC=CH) and the dihedral angle between the planes of the C=CH and HCC fragment [10], we estimated only roughly the dihedral angle between the $HC^{14}C^9C^4$ and $P^2C^3C^4C^9$ planes from analogous $^4J_{CP}$ coupling constant ($C^{14}C^9C$=CP). According to [10], the coupling constant $^4J_{CP}$ = 1.6 Hz corresponds to a dihedral angle of 270°, and $^4J_{CP}$ = 0.8 Hz, to 90°.



After removal of volatile compounds from the reaction mixture under reduced pressure (0.1 mm), the residue was subjected to hydrolysis in acetone; as a result, we isolated 2-hydroxy derivative **IV** (Scheme 2). Its mass spectrum (ES) contained the molecular ion peak with *m*/*z* 327 $[M + H]^+$ ($C_{14}H_9{}^{35}Cl_2O_3P$). The structure of compound **IV** was proved by the ^{31}P, ^1H, and ^{13}C NMR spectra using COSY ^1H–^1H and HETCOR ^1H–^{13}C correlation techniques. The data given in table indicate the cyclic structure of **IV**.

Scheme 2.



Thus the reaction of *o*-chlorophenylacetylene with 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole occurs under mild conditions and leads to the formation of 2,6-dichloro-4-(2-chlorophenyl)-1,2λ^5-benzoxaphosphinin-2-ones as a 1:1 mixture of two diastereoisomers due to the presence of a chiral phosphorus atom and restricted rotation about the C^4–C_{arom} bond.

EXPERIMENTAL

The NMR spectra were recorded on Bruker AC-300 (300, 75.47, and 121.47 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively), Bruker DRX-500 (500 and 125.7 MHz for ^{1}H and ^{13}C, respectively), and Bruker Avance-600 spectrometers (600 and 150.9 MHz for ^{1}H and ^{13}C, respectively). The chemical shifts were measured relative to tetramethylsilane (internal reference, ^{1}H and ^{13}C) or 85% H_3PO_4 (external reference, ^{31}P). The mass spectra (ES, MALDI-TOF) were obtained on a Kratos Compact MALDI II instrument (Shimadzu Europa GmbH, Duisburg, Germany) equipped with an N2-laser source (λ = 337 nm) (positive polarization, accelerating voltage 20 kV). The elemental compositions were determined on a Carlo Erba CHNS analyzer. The solvents were purified by standard procedures.

Reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (I) with 2-chlorophenylacetylene (II). A solution of 0.95 g (0.007 mol) of acetylene **II** in 2 ml of methylene chloride was added under stirring at 5–10°C to 1.0 g (0.0047 mol) of phosphole **I** in 10 ml of methylene chloride (the mixture was stirred by vigorously bubbling argon through a thin capillary). Argon was bubbled through the mixture for 3 h at 20°C, the solvent and excess acetylene **II** were removed under reduced pressure (0.1 mm) at 150°C, and the glassy residue (96%), a mixture of diastereoisomeric 2,6-dichloro-4-(2-chlorophenyl)-1,2λ^5-benzoxaphosphinin-2-ones **IIIA** and **IIIB**, was characterized by spectral methods. IR spectrum (film), ν, cm^{-1}: 1600, 1550, 1497, 1460, 1262, 1173, 1099, 1031, 962, 920, 821, 750, 706, 677. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 6.33 d (3-H, $^2J_{PH}$ = 23.6 Hz), 6.34 d (3-H, $^2J_{PH}$ = 23.0 Hz), 6.84 d (5-H, $^4J_{HH}$ = 2.3 Hz), 7.22 d (8-H, $^3J_{HH}$ = 8.7 Hz), 7.24 d (8-H, $^3J_{HH}$ = 8.7 Hz), 7.19 d.d (14-H, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.3–1.4 Hz), 7.31 d.d (14-H, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.3–1.4 Hz), 7.39 d.d (7-H, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.3 Hz), 7.37 m and 7.41 m (13-H), 7.43–7.44 m (12-H), 7.47 d.d (11-H, $^3J_{HH}$ = 7.9–8.0, $^4J_{HH}$ = 1.6), 7.51 d.d (11-H, $^3J_{HH}$ = 7.9–8.0, $^4J_{HH}$ = 0.5 Hz). ^{31}P–{^{1}H} NMR spectrum (121.49 MHz, $CDCl_3$): δ_P 17.2 and 17.1 ppm (two singlets, intensity ratio 1:1). Mass spectrum, *m*/*z*: 343 $[M - H]^+$, 345, 347. $C_{14}H_8{}^{35}Cl_3O_2P$. Calculated: *M* 344.

6-Chloro-4-(2-chlorophenyl)-2-hydroxy-1,2λ^5-benzoxaphosphinin-2-one (IV) was obtained by hydrolysis of diastereoisomer mixture **IIIA**/**IIIB** in diethyl ether. Yield 95%, mp 295–297°C. IR spectrum (KBr), ν, cm^{-1}: 3319, 2520–2960 s, v.br (POH), 2210–2320 s, v.br (POH), 1601, 1494, 1480, 1376, 1296, 1259, 1234, 1176, 1121, 1094, 1030, 972, 931, 865, 826, 758, 744, 723, 708, 595, 566. ^{1}H NMR spectrum, δ, ppm: in acetone-d_6 (500 MHz): 6.22 d (3-H, $^2J_{PH}$ = 15.5 Hz), 6.69 d (5-H, $^4J_{HH}$ = 2.6 Hz), 7.12 d (8-H, $^3J_{HH}$ = 8.7 Hz), 7.30 d.d.d (7-H, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.6, $^5J_{PH}$ = 1.2 Hz), 7.43 m (14-H, $^3J_{HH}$ = 9.3, $^4J_{HH}$ = 4.4 Hz), 7.50–7.52 m (12-H, 13-H), 7.58 m (11-H, $^3J_{HH}$ = 9.3, $^4J_{HH}$ = 4.8 Hz); in methanol-d_4 (500 MHz): 6.33 d (3-H, $^2J_{PH}$ = 16.8 Hz), 6.78 d (5-H, $^4J_{HH}$ = 2.5 Hz), 7.29 d (8-H, $^3J_{HH}$ = 8.7 Hz), 7.47 br.d.d (7-H, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.5 Hz), 7.48 m (14-H), 7.56–7.57 m (12-H, 13-H), 7.58 m (11-H, $^3J_{HH}$ = 9.3, $^4J_{HH}$ = 4.8 Hz); in DMSO-d_6–acetone-d_6, 1:4 (600 MHz): 6.24 d (3-H, $^2J_{PH}$ = 16.3 Hz), 6.68 d (5-H, $^4J_{HH}$ = 2.6 Hz), 7.29 d (8-H, $^3J_{HH}$ = 8.8 Hz), 7.44 d.d.d (7-H, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.6, $^5J_{PH}$ = 1.3 Hz), 7.57 d.d (11-H, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.4 Hz), 7.51 d.d.d (12-H, $^3J_{HH}$ = 7.9, 7.2, $^4J_{HH}$ = 1.8 Hz), 7.49 d.d.d (13-H, $^3J_{HH}$ = 7.2, 7.5, $^4J_{HH}$ = 1.4 Hz), 7.40 d.d (14-H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.8 Hz). ^{31}P–{^{1}H} NMR spectrum (121.49 MHz, acetone-d_6): δ_P 1.6 ppm, s. Mass spectrum, *m*/*z*: 327 $[M + H]^+$, 329, 331. Found, %: C 58.44; H 2.81; P 9.37. $C_{14}H_9{}^{35}Cl_2O_3P$. Calculated, %: C 51.38; H 2.75; P 9.48.

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