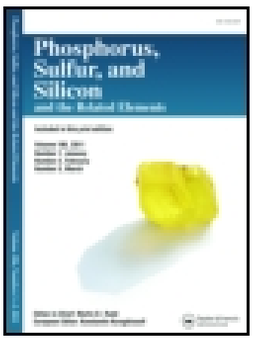

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Phosphorus, Sulfur, and Silicon and the Related Elements

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THE INTERACTION OF 2-(5-METHYL-2-PHENYL-2H-1,2,3-DIZAPHOSPHOL-4-YL)-4H-BENZO[e]-1,3,2-DIOXAPHOSPHININ-4-ONE WITH ACTIVATED CARBONYL COMPOUNDS. SYNTHESIS OF BIS-HETEROCYCLIC SYSTEMS CONTAINING DI- AND TETRACOORDINATED PHOSPHORUS

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THE INTERACTION OF 2-(5-METHYL-2-PHENYL-2*H*-1,2,3-DIZAPHOSPHOL-4-YL)-4*H*-BENZO[*e*]-1,3,2-DIOXAPHOSPHININ-4-ONE WITH ACTIVATED CARBONYL COMPOUNDS. SYNTHESIS OF BIS-HETEROCYCLIC SYSTEMS CONTAINING DI- AND TETRACOORDINATED PHOSPHORUS

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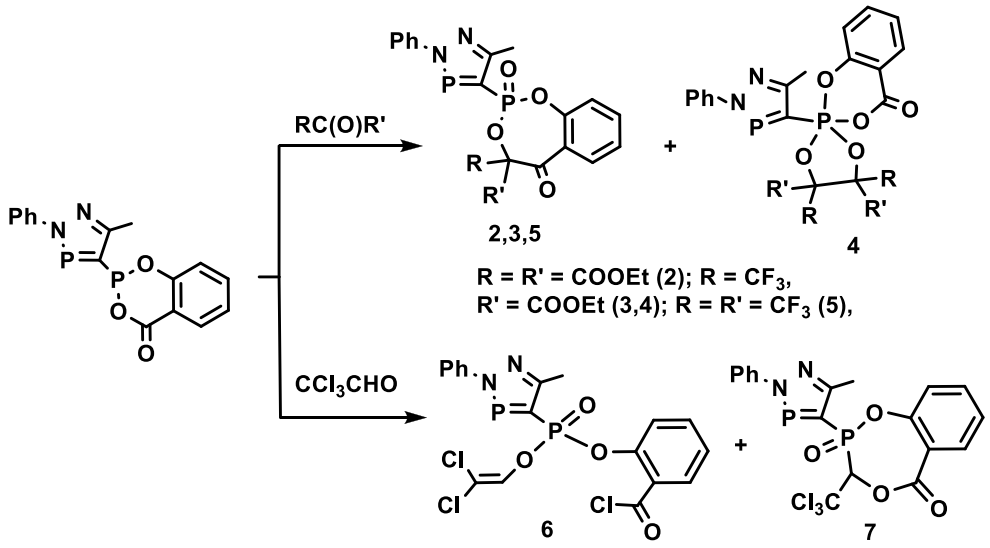
Abstract

The interaction of 2-(5-methyl-2-phenyl-2*H*-1,2,3-dizaphosphol-4-yl)-4*H*-benzo[*e*]-1,3,2-dioxaphosphinin-4-one with mesoxalic and trifluoropyruvic acids ethyl and diethyl esters, hexafluoroacetone and chloral proceeds with an exclusive participation of P(III) atom and allows to obtain 2-(5-methyl-2-phenyl-2*H*-1,2,3-dizaphosphol-4-yl)-derivatives of 1,4,2- and 1,3,2-dioxaphosphepines as well as dichlorovinylphosphonate, being the product of Perkow reaction in the case of chloral.

Graphical Abstract



Keywords

Diazaphosphole; benzodioxaphosphinine; benzodioxaphosphepine; chloral; hexafluoroacetone; Perkow reaction.

Introduction

Organophosphorus heterocycles have a high theoretical and practical importance.[1-6] Among the wide range of phosphorus-containing heterocycles the reactive trivalent phosphorus species play a role of precursors in the synthesis of tetracoordinated phosphorus derivatives, which are usually very stable.[3-9] The cyclic mixed anhydrides, obtained from hydroxy/aminocarboxylic acids and phosphoric / phosphonic acids contain a nucleophilic phosphorus(III) atom as well as electrophilic carbonyl group and occupy a special position among trivalent phosphorus heterocycles. The presence of macroergic P(III)–O–C(O)/P(III)–N(R)–C(O) fragment in the initial phosphite molecule leads to an appearing of unusual reactivity, namely, to the possibility that both P(III) atoms react with nucleophiles and electrophiles, affording a diverse range of heterocycles containing tetracoordinated phosphorus.[10-16]

Functionalization of the exocyclic substituent, bonded to the phosphorus(III) atom, by additional introduction of heterocyclic fragments could lead to new directions, such as cascade processes allowing to involve both heterocyclic systems into reactions.[17-19]

In this article the 1,2,3-diazaphospholyl substituent, bearing nucleophilic two-coordinated phosphorus atom ($\sigma^2\lambda^3$), was chosen as a second heterocyclic fragment R and was included in the 2-R-benzo[*e*]-1,3,2-diheterophosphinin-4-one molecule containing a P($\sigma^3\lambda^3$)-atom. The literature data gives for diazaphospholes evidence of high reactivity in various reactions. Substitution at carbon, alkylation and substitution at nitrogen or phosphorus, 1,2-additions to C=P- or N=P-bond and oxidative addition to phosphorus, cycloaddition reactions, including [2+3]-, [1+4]- and [2+4]-cycloadditions, as well as the coordination to transition metals should be mentioned

among them.[20-27] The frontier orbital crossing calculations showed the ambident reactivity of P($\sigma^2\lambda^3$) systems, containing a P=X double bond.[28]

The chemical properties of diazaphospholes bearing exocyclic phosphorus atom as a substituent (with the coordination numbers of 2 and 4, 2 and 3, 2 and 5 as well as 2 and 6) are reviewed.[29] It is known that some reactions of diazaphospholes like interaction with proton donors appeared to be reversible.[30,31] Nevertheless, the information concerning competitive and cascade reactions of bis-heterocyclic P^{II},P^{III}-systems with activated carbonyl compounds is absent.

The presence of a nucleophilic P($\sigma^2\lambda^3$)-atom in the diazaphosphole molecule can change not only the reaction pathways in the reaction with various reagents, but also the reactivity of the P($\sigma^3\lambda^3$)-mojety.

Results and Discussion

The approach to the synthesis of bis-heterocyclic polyfunctional 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*e*]-1,3,2-dioxaphosphinin-4-one **1**, combining the 5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphole and benzo[*e*]-1,3,2-dioxaphosphinin-4-one fragments was realized in this work. It is based on the reaction of the 1-trimethylsilyloxy-2-trimethylsilyloxycarbonylbenzene with 4-(dichlorophosphino)-5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphole occurring at room temperature. The 1,3,2-dioxaphosphinin-4-one **1** was obtained by the procedure, similar to 4-(dichlorophosphino)-2,5-dimethyl-2*H*-1,2,3-diazaphosphole.[32-33] Compound **1** appeared to be stable and does not undergo any transformations at room temperature. The structure of the isolated phosphonite **1** was proved by spectroscopic methods.

The $^{31}P\{^{1}H\}$NMR spectrum contains two doublets with δ_P 238.5 (P^{II}) and 156.3 (P^{III}) ($^{2}J_{PCP}$ = 16.6 Hz), the low field doublet of P^{II} being broadened. The ^{13}C and $^{13}C\{^{1}H\}$ NMR spectra contain characteristic carbon signals, showing couplings with one or two phosphorus atoms. The multiplicity of the C^{4b} signal, belonging to the diazaphosphole cycle (d.d) is in agreement with the formation of the P=C^{4b}–P fragment (δ_C 148.5, $^{1}J_{PC}$ 63.5 Hz, $^{1}J_{PC}$ 56.1 Hz); the signals of C^{4a} (δ_C 116.1, $^{3}J_{POCC}$ 11.7 Hz, $^{5}J_{PCPOCC}$ 3.3 Hz) and C^{5b} (δ_C 158.4, $^{2}J_{PCC}$ 23.8 Hz, $^{2}J_{PCC}$ 5.5 Hz) are also doublets of doublets. The XRD data confirms also the molecular structure of compound **1** (Figure 1).

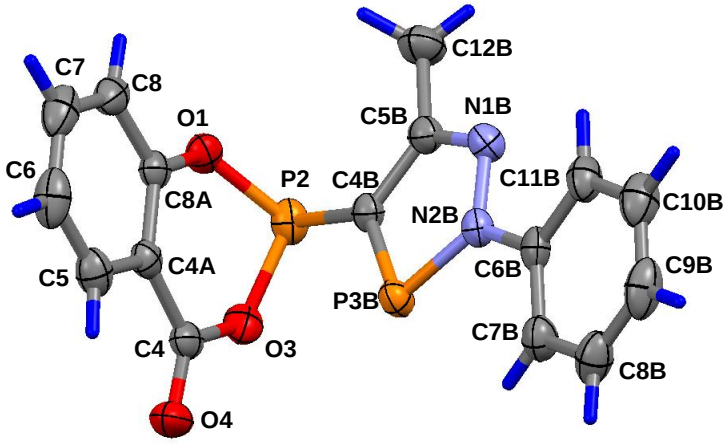


Figure 1. Molecular structure in the crystal and atom labeling scheme for **1** (30 % thermal ellipsoids). Selected bond lengths (Å), bond and torsion angles (°): P(2)–O(1) 1.639(2), P(2)–O(3) 1.658(2), P(2)–C(4B) 1.801(2), P(3B)–N(2B) 1.688(2), P(3B)–C(4B) 1.704(2), O(1)–C(8A) 1.376(3), O(3)–C(4) 1.367(3), O(4)–C(4) 1.196(4), N(1B)–N(2B) 1.354(3), N(1B)–C(5B) 1.317(3), C(4)–C(4A) 1.468(3), C(4B)–C(5B) 1.414(3), O(1)–P(2)–O(3) 99.87(8), O(1)–P(2)–C(4B) 103.05(9), N(2B)–P(3B)–C(4B) 89.1(1), P(2)–O(1)–C(8A) 120.2(1), P(2)–O(3)–C(4)

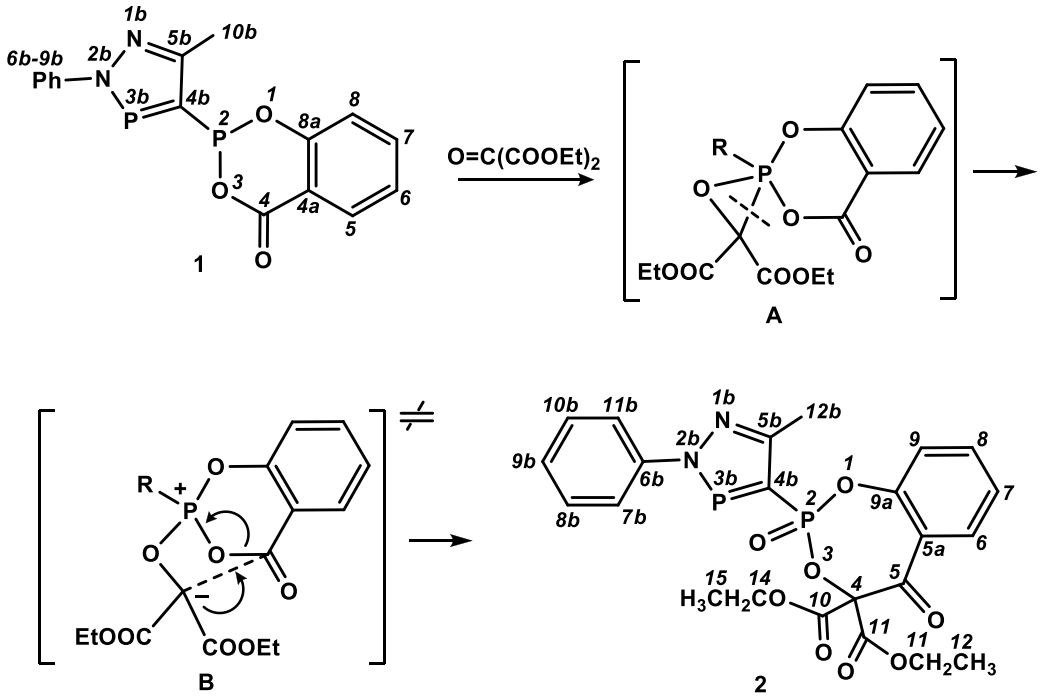
124.5(2), N(2B)–N(1B)–C(5B) 108.9(2), P(3B)–N(2B)–N(1B) 116.6(1), C(4)–C(4A)–C(8A) 122.4(2), P(2)–C(4B)–P(3B) 126.7(2), P(2)–C(4B)–C(5B) 123.5(2), N(1B)–C(5B)–C(4B) 116.2(2), P(3B)–C(4B)–C(5B) 109.3(2), C(4B)–P(2)–O(3)–C(4) 68.1(2), C(4B)–P(2)–O(1)–C(8A) –59.4(2), O(3)–P(2)–O(1)–C(8A) 42.1(2), O(1)–P(2)–O(3)–C(4) –36.9(2), O(1)–P(2)–C(4B)–P(3B) 113.8(2), O(1)–P(2)–C(4B)–C(5B) –76.1(2), O(3)–P(2)–C(4B)–P(3B) 11.5(2), O(3)–P(2)–C(4B)–C(5B) –178.4(2), C(7B)–C(6B)–N(2B)–N(1B) –169.8(2), C(11B)–C(6B)–N(2B)–P(3B) –166.0(2).

According to the literature data, mentioned above, we suggested that the molecule of compound **1**, bearing P^{II} and P^{III} atoms with different lone pairs of electrons, would easy react with electron deficient carbonyl compounds like hexafluoroacetone, chloral or ethyl ester of mesoxalic and trifluoropyruvic acids. 5-Phenyl-5-methyl-1,2,3-diazaphosphole acts as nucleophile with the highly electrophilic hexafluoroacetone, resulting in fluorinated diazaphosphole derivatives.[2,34] On the other side, 2-R-benzo[*e*]-1,3,2-dioxaphosphinin-4-ones easily react with the electrophiles mentioned above, leading to ring enlargement products (from six- to seven membered heterocycles) as well as to products with pentacoordinated phosphorus – phosphoranes.[35,36] Firstly, the nucleophilic attack of the phosphorus atom to the activated carbon atom takes place. It involves the intermediate formation of spirophosphoranes, containing oxaphosphirane cycle.[37]

Compound **1** proved to be more stable to oxidation in comparison with 5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphole and 2-Ph-benzo[*e*]-1,3,2-dioxaphosphinin-4-one. Derivative **1** was proved to be less reactive to the activated reagents, mentioned above. In all cases the two-

coordinated phosphorus atom ($\sigma^2\lambda^3$) remains intact. Taking into account published data[38] it can be assumed, that introduction of the sterically hindered and at the same time weakly electron withdrawing benzo[*e*]-1,3,2-dioxaphosphinin-4-one substituent in 4 position of diazaphosphole changes the electronic situation at the phosphorus atom of the latter. This means, that the lone pair of electrons becomes less convenient for the attack by an electrophile. The diazaphosphole fragment in turn is sterically hindered and possesses a weak electron withdrawing effect as well. It also influences the chemoselectivity of the P($\sigma^3\lambda^3$) atom, belonging to the benzo[*e*]-1,3,2-dioxaphosphinin-4-oxide.[39]

The 2-R-benzo[*e*]-1,3,2-dioxaphosphinin-4-one derivatives usually react with mesoxalic acid diethyl ester giving the phosphorane derivatives without the participation of the P^{III}–OC(O) bond.[40] The interaction of 2-isocyanatobenzo[*e*]-1,3,2-dioxaphosphinin-4-one with mesoxalic acid diethyl ester yields products with bicyclononane structure.[41] Compound **1** was found to react with mesoxalic acid diethyl ester with the formation of 1,3,2-dioxaphosphepine **2**. The possible intermediate, bearing a three-membered cycle (**A**), is the product of the cheletropic reaction of the phosphorus atom with the carbonyl group. It transforms further *via* betaine-like transition state (**B**) into the 1,3,2-dioxaphosphepine **2** (Scheme 1).



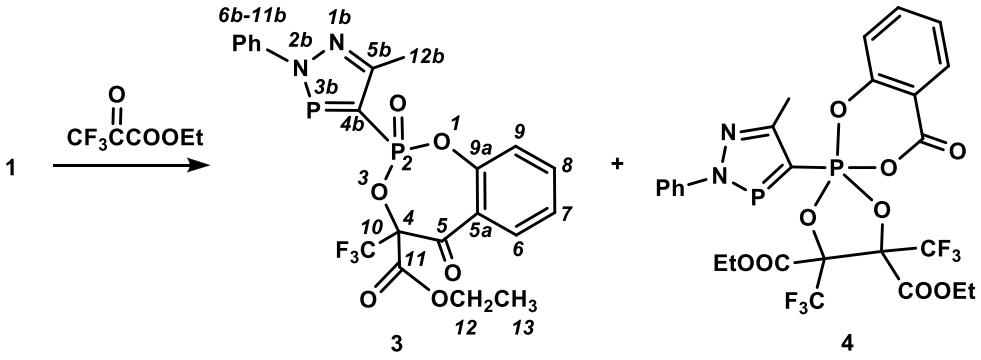
Scheme 1. The reaction of phosphonite **1** with mesoxalic acid diethyl ester.

The structure of **2** was identified by ^{1}H, ^{13}C, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectroscopy. The $^{31}P\{^{1}H\}$ NMR spectrum contains two doublets with δ_P 251.3 (br. d) and 14.9 (d, $^{2}J_{PCP}$ 76.3 Hz). The $^{13}C\{^{1}H\}$ NMR spectrum displays the characteristic upfield (δ_C 88.6, $^{2}J_{POC}$ 8.3 Hz) and lowfield (δ_C 185.3) signals belonging to the carbon atoms (C^4 and C^5) of 1,3,2-dioxaphosphepine cycle. Interpretation of ^{13}C NMR spectra is made taking into account published data.[24,32]

Thus, 5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl substituent is likely to direct the reaction by the pathway, that is non-characteristic for diethyl ester of mesoxalic acid. This pathway includes the ring enlargement reaction from a six-membered to a seven-membered P-heterocycle with high chemo- and regioselectivity. The formation of 1,3,2-dioxaphosphepine

derivative **2** is the only direction of this reaction, and the two-coordinated phosphorus atom does not take part in the process.

The reaction of compound **1** with trifluoropyruvic acid ethyl ester proceeds by two pathways (Scheme 2). The main pathway (> 90 %) includes the formation of 1,3,2-dioxaphosphepine **3**, which is the P–CO → P–OC rearrangement product. Such a behavior of compound **1** also differs from the similar reaction of 2-R-benzo[*e*]-1,3,2-dioxaphosphinin-4-one with trifluoropyruvic acid ethyl ester leading to spirophosphoranes.[16,42] The minor pathway (< 8 %) includes the formation of pentacoordinated phosphorus derivative **4**, showing characteristic signals in $^{31}P\{^{1}H\}$ NMR spectrum: –32.3 d, –34.1 d (5 : 1) (P^{IV}), 254.0 br. d (P^{II}) ($^{2}J_{PCP}$ 87.2 Hz).

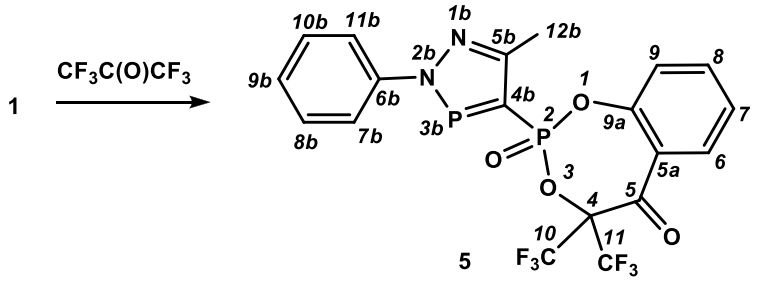


Scheme 2. The reaction of phosphonite **1** with ethyl ester of trifluoropyruvic acid.

Trifluoropyruvic acid ethyl ester contains prochiral carbonyl group which converts into C^{4}-asymmetric center during the reaction process. This leads to the formation of two diastereoisomers of compound **3** in the ratio of 55 to 45. Their structures were confirmed by the NMR spectroscopy and mass spectrometry. The phosphepine **3** was washed free from

phosphorane **4** impurities and dried of volatile compounds. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of compound **4** contain the double set of signals with closely related integral intensities, which does not allow the a detailed correlation to each diastereoisomer. The $^{31}P\{^{1}H\}$ NMR spectrum contains three doublets with corresponding coupling constants through two bonds: δ_P 252.1 (br. d) and δ_P 12.4 (d, $^{2}J_{PCP}$ 74.1 Hz), 250.1 (br. d) and δ_P 16.1 (d, $^{2}J_{PCP}$ 82.3 Hz).

The reaction of compound **1** with hexafluoroacetone leads to the formation of 1,3,2-dioxaphosphepine derivative **5** (Scheme 3). The structure of compound **5** was proved by NMR and IR spectroscopy. The $^{13}C\{^{1}H\}$ NMR spectrum contains characteristic signals for C^4 and C^5 (δ_C 83.6 and 185.5 ppm), which definitely agree with the 1,3,2-dioxaphosphepine structure. The characteristic doublet with δ_P 252.9 ppm ($^{2}J_{PCP}$ 82.8 Hz) in the $^{31}P\{^{1}H\}$ NMR spectrum indicates that the P^{II}-fragment of the molecule has not changed, despite an excess of hexafluoroacetone and prolonged exposure. This result may be caused by the presence of the bulky six-membered heterocycle at C^{4b} as well as by the high energetic benefit of the phosphoryl group formation from the $P(\sigma^3\lambda^3)$-atom. The structure of compound **5** was confirmed by single crystal X-ray diffraction studies (Figure 2).



Scheme 3. The reaction of phosphonite **1** with hexafluoroacetone.

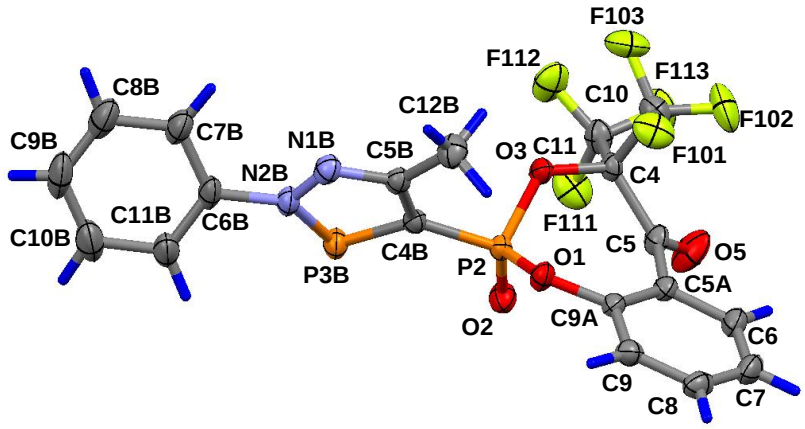
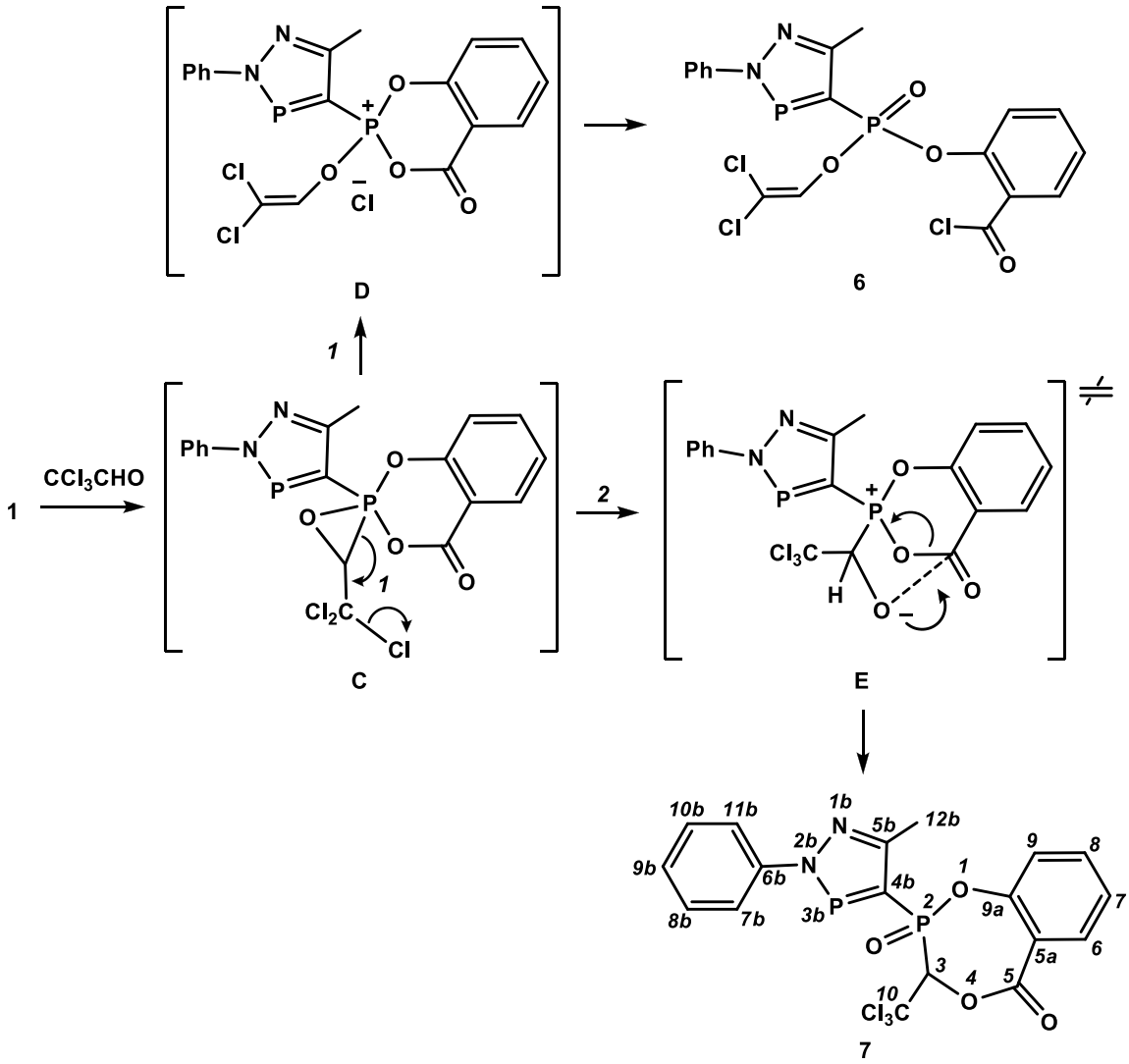


Figure 2. Molecular structure in the crystal and atom-labeling scheme for **5** (30 % thermal ellipsoids). Selected bond lengths (Å), bond and torsion angles (°): P(2)–O(1) 1.587(2), P(2)–O(2) 1.446(2), P(2)–O(3) 1.602(2), P(2)–C(4B) 1.748(3), P(3B)–N(2B) 1.676(3), P(3B)–C(4B) 1.711(3), O(1)–C(9A) 1.394(3), O(3)–C(4) 1.418(3), O(5)–C(5) 1.205(4), N(1B)–N(2B) 1.364(3), N(1B)–C(5B) 1.323(3), N(2B)–C(6B) 1.438(3), C(4)–C(5) 1.556(4), C(4B)–C(5B) 1.418(3), C(5)–C(5A) 1.495(4), O(2)–P(2)–O(1) 114.7(1), O(2)–P(2)–O(3) 113.5(1), O(1)–P(2)–O(3) 101.9(1), O(2)–P(2)–C(4B) 117.5(1), O(1)–P(2)–C(4B) 104.1(1), O(3)–P(2)–C(4B) 103.4(1), N(2B)–P(3B)–C(4B) 88.3(1), C(9A)–O(1)–P(2) 123.4(1), C(4)–O(3)–P(2) 122.5(1), C(5B)–N(1B)–N(2B) 109.0(2), N(1B)–N(2B)–C(6B) 117.7(2), N(1B)–N(2B)–P(3B) 117.4(2), C(6B)–N(2B)–P(3B) 124.88(19), C(5B)–C(4B)–P(3B) 110.7(2), C(5B)–C(4B)–P(2) 127.9(2), P(3B)–C(4B)–P(2) 121.5(2), N(1B)–C(5B)–C(4B) 114.6(2), N(1B)–C(5B)–C(12B) 118.8(2), O(2)–P(2)–O(1)–C(9A) 48.8(2), O(3)–P(2)–O(1)–C(9A) –74.3(2), O(1)–P(2)–O(3)–C(4) 77.2(2), C(4B)–P(2)–O(3)–C(4) –175.1(2), O(1)–P(2)–C(4B)–P(3B) –135.8(1), O(2)–P(2)–C(4B)–P(3B) –7.8(2), O(1)–P(2)–C(4B)–C(5B) 43.4(2), O(2)–P(2)–C(4B)–C(5B) 171.4(2), C(7B)–C(6B)–N(2B)–N(1B) 38.8(3), C(11B)–C(6B)–N(2B)–P(3B) 40.6(3).

The reaction of chloral with compound **1** (20 °C) is different from the one with 2-R-4*H*-benzo[*e*]-1,3,2-dioxaphosphinin-4-one.[35] It proceeds by two pathways including Perkow reaction (pathway ***1***) and ring enlargement reaction (pathway ***2***) (Scheme 4). The first pathway leads to the formation of dichlorovinylphosphonate **6** and the second one gives the benzo[*f*]-1,4,2-dioxaphospepine **7** in a ratio of 9 : 1. The last compound was obtained as a mixture of diastereoisomers in a 2 : 1 ratio (δ_P 246.1, br. d, δ_P 26.0 d, $^2J_{PCP}$ 65.7 Hz; δ_P 246.1 br. d, δ_P 29.6 d, $^2J_{PCP}$ 68.1 Hz).

The reaction seems to begin with [1+2]-cycloaddition of the P^{III} atom to chloral with formation of the intermediate spirophosphorane bearing three-membered cycle (**C**). According to Perkow mechanism, the heterocycle (**C**) eliminates chloride-anion and forms intermediate quasiphosphonium salt (**D**). Susequently cleavage of the cyclic $P^{III}O$–C(O) bond in the intermediate (**D**) takes place resulting in the final reaction product **6** (pathway ***1***). The second pathway involves the formation of the species (**C**) and its transformation to the reaction product **7** *via* a betaine-like transition state (**E**). The phosphepine **7** was gradually crystallized from the reaction mixture and isolated.



Scheme 4. The reaction of phosphonite **1** with chloral.

The introduction of diazaphosphole fragment as exocyclic substituent increases the sensibility of the compound **1** towards hydrolysis and various transformations during storage. Compound **6** remains as non-distillable oil after filtration of the reaction mixture from phosphepine **7**. The structure of **6** was established by NMR spectroscopy. The $^{31}P\{^{1}H\}$ NMR

spectrum contains signals at δ_P 251.9 (br. d) and δ_P 11.3 (d), $^2J_{PCP}$ 84.5 Hz. Thus, P^{II}-fragment of the molecule **1** remains inactive in this reaction, but strongly affects its synthetic result. It guides the reaction with chloral predominantly on the way to the dichlorovinylphosphonate **6** (Perkow pathway).

Crystallization allows to isolate the major isomer of 1,4,2-dioxaphosphepine **7**. The structure of this compound was established by NMR spectroscopy and single crystal X-ray diffraction studies. The geometry of the molecule **7** is shown in Figure 3.

The X-ray structure of compound **7** was published earlier in our preliminary communication[43] without a detailed discussion. Here comparative analysis of the structures of the three compounds synthesized (**1**, **5**, **7**) is presented. There is one independent molecule of each compound in the asymmetrical unit.

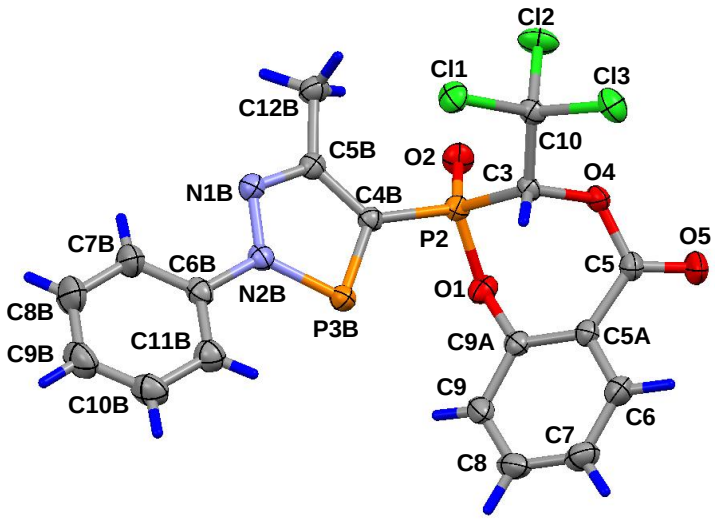


Figure 3. The molecular structure of phosphepine **7** in the crystal (30 % of thermal ellipsoids). P2–O1 1.596(2), P2–O2 1.462(2), P2–C3 1.853(2), P2–C4B 1.763(2), P3B–N2B 1.684(2), P3B–

C4B 1.715(2), O1–C9A 1.395(3), O4–C3 1.435(3), O4–C5 1.365(3), O5–C5 1.194(3), N1B–N2B 1.359(3), N1B–C5B 1.323(3), N2B–C6B 1.435(3), C3–C10 1.528(3), C4B–C5B 1.423(3), C5–C5A 1.480(3), C5A–C6 1.395(4), C5A–C9A 1.381(3), C5B–C12B 1.497(4), O1–P2–O2 110.6(1), O1–P2–C3 98.27(9), O1–P2–C4B 105.8(1), O2–P2–C3 114.7(1), O2–P2–C4B 115.7(1), N2B–P3B–C4B 88.7(1), P2–O1–C9A 129.2(2), N2B–N1B–C5B 109.3(2), P3B–N2B–N1B 117.0(2), P3B–N2B–C6B 125.4(2), N1B–N2B–C6B 117.6(2), P2–C3–O4 105.3(1), P2–C3–C10 118.9(2), O4–C3–C10 105.9(2), P2–C4B–P3B 124.2(1), P2–C4B–C5B 125.9(2), P3B–C4B–C5B 109.9(2), N1B–C5B–C4B 115.1(2), O2–P2–O1–C9A 152.3(2), C3–P2–O1–C9A 31.9(2), O1–P2–C4B–P3B 26.7(2), P3B–N2B–C6B–C7B 15.4(3), O2–P2–C3–C10 56.9(2).

Diazaphosphole heterocycle of molecules **1**, **5**, **7** is planar (within 0.007(2) Å for **1**, within 0.003(2) Å for **5**, within 0.000(2) Å for **7**, respectively). The deviations of P(2) and C(12b) atoms from the plane of the heterocycle are rather small (**1**: P(2) –0.189(1) Å, C(12b) –0.012(4) Å; **5**: P(2) 0.032(1) Å, C(12b) –0.002(4) Å; **7**: P(2) –0.037(1) Å, C(12b) –0.007(3) Å); that is why all those atoms can be considered lying in heterocycle plane with the only exception of P(2) atom in molecule **1**. Dihedral angles between the phenyl substituent and diazaphosphole plane are: 12.1(1)° in **1**, 39.5(1)° in **5**; 14.8(2)° in **7**. The largest value of corresponding dihedral angle for **5** is probably caused by the presence of sterically hindered benzodioxaphosphepine fragment. In molecules **5** and **7** the configuration of the other phosphorus atom is tetrahedral, whereas it is pyramidal one in molecule **1**.

In molecule **1** the six-membered phosphorus heterocycle adopts the conformation of a P-*envelope*: the atom P(2) deviates from the O(1)C(8a)C(4a)C(4)O(3) plane (planar within

0.052(2) Å) by 0.5918(6) Å. The dioxaphosphepine heterocycle in molecule **5** adopts a *twist-boat* conformation (the heteroatom fragment O(1)C(5a)C(9a)C(5) is planar within 0.002 (2) Å. The atoms P(2) and C(4) deviate from this plane on one side by 0.5318(6) and 0.792(2) Å, the O(3) atom deviates to the opposite side by –0.643(1) Å). Molecule **7** has a conformation of a distorted *boat* (the fragment O(1)C(5a)C(9a)C(5) is planar within 0.010(2) Å, the atoms P(2), C(3) and O(4) deviate from this plane on one side by –1.1531(5), –1.853(2) and –0.744(2) Å respectively).

The crystal structure of **1**, **5** and **7** is stabilized mainly by C–H···O- hydrogen bonds and π–π-interactions.

In the crystal the molecules of compounds **1** and **7** form the infinite chains along the *a* crystallographic axis (see the Supporting Information file) due to short interactions of C–H···O-type. The parameters of the interactions are: in **1** bifurcate interaction C(8)–H(8)···O(4), C–H 0.90(3) Å, H···O 2.58(3) Å, C···O 3.405(5) Å, ∠CHO 152(2)°, symmetry operation 1 + *x*, *y*, *z*; and C(12b)–H(122)···O(4), C–H 0.98(3) Å, H···O 2.60(3) Å, C···O 3.560(5) Å, ∠ CHO 168(3)°, symmetry operation 1 + *x*, *y*, *z*; in **7** C(3)–H(3)···O(2), C–H 0.89(2) Å, H···O 2.42(2) Å, C···O 3.282(3) Å, ∠ CHO 162(2)°, symmetry operation 1 + *x*, *y*, *z*.

In the crystal of compound **5** the sterically hindered benzodioxaphosphepine fragment causes the formation of molecular dimers, instead of molecular chains like in **1** and **7** (see the Supporting Information file). Parameters of the short C(6)–H(6)···O(5)-interaction in **5** are: C–H 0.98(3) Å, H···O 2.56(3) Å, C···O 3.325(5) Å, ∠CHO 135(2)°, symmetry operation –*x*, 1 – *y*, 1 – *z*. It is interesting to note an alternation of diazaphosphole cycle with phenyl substituent and dioxaphosphepine cycle in the crystal of **5** (see the Supporting Information file). The packing of

the molecules in the crystal is also stabilized by π–π-interactions between C(5a-9a) phenyl substituents. The distance between the centers of the rings is d_c 3.810(4) Å, the dihedral angle between the corresponding planes is α = 12.9°, the shortest distance between the planes is $d_\perp$ – 3.26 Å.

Conclusions

Thus, the ability of bis-heterocyclic 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*e*]-1,3,2-dioxaphosphinin-4-one **1** to react with only one molecule of an activated carbonyl compound was shown in this work. The synthetic result of the reaction is defined by the sterical and electronic properties of the exocyclic diazaphosphole substituent at the phosphorin-4-onic phosphorus atom. The regiochemistry of the reaction with hexafluoroacetone appears to be the same as in the case of 2-R-benzo[*e*]-1,3,2-dioxaphosphinin-4-ones (phosphepine pathway). The reaction of compound **1** with esters of mezoxalic and trifluoropyruvic acids leads to phosphepines as the result of phosphonate-phosphate rearrangement instead of the expected phosphoranes. It was found, that the main pathway for the interaction of chloral with compound **1** is a Perkow reaction. In all cases the two-coordinated phosphorus atom remains unchanged.

Experimental

General

Melting points were measured with a Stuart digital SMP10 apparatus. Mass spectra were recorded with a DFS Thermo Electron Corporation instrument (Germany). The energy of

ionizing electrons was 120 eV and the temperature of ion source was 200 °C. The system of direct input of substances into the source was used. The temperature of the ampoule and evaporation ranged from 50 °C to 350 °C. The IR spectra were measured with a Bruker Vector-22 instrument in KBr pellets. NMR spectra were recorded with a Bruker Avance-400 instrument (400 MHz for ^{1}H and 100.6 MHz for ^{13}C) in $CDCl_3$ as a solvent. Chemical shifts are given in ppm (δ) relative to residual $CHCl_3$ signal and coupling constants (*J*) are reported in Hertz (Hz). The elemental analyses were obtained with a Euro Vector-3000 analyzer (C, H, N) and by burning in a stream of oxygen (Cl, P).

X-ray crystallography

Single crystal XRD experiments were carried out with a Bruker Smart APEX II automatic diffractometer with a two-dimensional CCD detector at a temperature of 293 K (λMoK_α, graphite monochromator, λ = 0.71073 Å, ω-scan mode). Absorption correction was carried out using the SADABS program.[44] The structure was solved by the direct methods and refined first in an isotropic and then anisotropic approximation using the SHELXL-97[45] and WinGX[46] programs. The hydrogen atoms were found from difference Fourier maps and refined isotropically. Data collection, unit cell parameters, indexation and refinement were processed using the APEX2 software.[47] The unit cell parameters, coordinates of the atoms and their temperature parameters have been deposited with the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk) under no. CCDC 862209 and 862208 for the compounds **1** and **5**, respectively. Crystallorgaphic data of **7** have been reported previously.[43] The analysis of the intermolecular interactions and the figures were made using the PLATON[48] and ORTEP[49]

programs.

Compound **1** ($C_{16}H_{12}N_2O_3P_2$): triclinic, space group *P*-1, a = 7.521(2), b = 8.013(2), c = 15.325(5) Å, α = 77.964(4), β = 76.862(3), γ = 62.285(2)°, V = 790.5(4) Å^3, M = 342.22, d_{calc} = 1.438 g/cm^3, Z = 2. Cell parameters and intensities of 7928 reflections, including 3076 independent reflections, 2440 of which had $I \geq 2\sigma$ (R_{int} = 0.0233), were measured at a temperature of 293 K (2.75° ≤ θ ≤ 26.00°, index ranges: –9 ≤ h ≤ 9, –9 ≤ k ≤ 9, –18 ≤ l ≤ 18). The absorption coefficient μMo = 2.90 cm^{-1}, F (000) = 352. The final divergence factors are R = 0.0369, R_w = 0.1124 from 2440 reflections with $F^2 \geq 4\sigma$; the goodness-of-fit parameter is 0.841, 256 refined parameters.

Compound **5** ($C_{19}H_{12}F_6N_2O_4P_2$): monoclinic, space group $P2_1/c$, a = 20.499(17), b = 14.456(12), c = 6.955(6) Å, β = 91.20(1)°, V = 2060(3) Å^3, M = 508.25, d_{calc} = 1.638 g/cm^3, Z = 4. Cell parameters and intensities of 15238 reflections, including 4046 independent reflections, 2941 of which had $I \geq 2\sigma$ (R_{int} = 0.0467), were measured at a temperature of 293 K (1.99° ≤ θ ≤ 26.00°, index ranges: –25 ≤ h ≤ 24, –17 ≤ k ≤ 17, –8 ≤ l ≤ 8). The absorption coefficient μMo = 2.96 cm^{-1}, F (000) = 1024. The final divergence factors are R = 0.0437, R_w = 0.1005 from 2941 reflections with $F^2 \geq 4\sigma$; the goodness-of-fit parameter is 1.035, 346 refined parameters.

Syntheses and spectroscopic data

2-(5-Methyl-2-phenyl-2H-1,2,3-diazaphosphol-4-yl)-4H-benzo[e]-1,3,2-dioxaphosphinin-4-one **(1)**

4-(Dichlorophosphino)-5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphole (4.28 g, 0.015 mol) was added to a mixture of 1-trimethylsilyloxy-2-trimethylsilyloxycarbonylbenzene (4.36 g, 0.015 mol) and CH_2Cl_2 (3 mL) in argon atmosphere. The reaction mixture was dried *in vacuo* (1.5 Torr) and 4.77 g (93 %) of a light-yellow powder was isolated. Compound **1** thus obtained was used without further purification. m.p. 97-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (dd, $^{3}J_{HCCH}$ = 8.0, $^{4}J_{HCCCH}$ = 1.9, 1H, H-5), 7.30 (dd, $^{3}J_{HCCH}$ = 7.6, $^{3}J_{HCCH}$ = 6.6, 1H, H-6), 7.59 (ddd, $^{3}J_{HCCH}$ = 7.6, $^{3}J_{HCCH}$ = 8.3, $^{4}J_{HCCCH}$ = 1.6), 7.10 (d, $^{3}J_{HCCH}$ = 8.2, 1H, H-7, 1H, H-8), 7.66 (dd, $^{3}J_{HCCH}$ = 8.5, $^{4}J_{PNCCH}$ = 1.6, 1H, H-7b), 7.38 (dd, $^{3}J_{HCCH}$ = 8.6, $^{3}J_{HCCH}$ = 6.7, 1H, H-8b), 7.20 (td, $^{3}J_{HCCH}$ = 7.6, $^{4}J_{HCCCH}$ = 2.0, 1H, H-9b), 2.69 (s, 1H, H-12b). ^{13}C NMR (100.6 MHz, $CDCl_3$): (hereinafter the splitting of the signal in the $^{13}C\{^{1}H\}$ NMR spectrum is given in parentheses), δ = 162.3 dd (br. s) ($^{2}J_{P^2OC^4}$ = 1.5, $^{3}J_{HC^5CC^4}$ = 8.4, C-4), 118.1 dd (m) ($^{3}J_{P^2OCC^{4a}}$ = 12.0, $^{5}J_{P^{3b}CPOCC^{4a}}$ = 3.6, C-4a), 131.5 ddddd (d) ($^{1}J_{HC^5}$ = 165.6, $^{3}J_{HC^7CC^5}$ = 8.3, $^{4}J_{P^2OCCC^5}$ = 2.2, $^{2}J_{HC^6C^5}$ = 2.1-2.2, $^{4}J_{HC^8CCC^5}$ = 1.0, C-5), 124.6 dd (s) ($^{1}J_{HC^6}$ = 164.0, $^{3}J_{HC^8CC^6}$ = 7.9, C-6), 136.9 dddd (d) ($^{1}J_{HC^7}$ = 161.7, $^{3}J_{HC^5CC^7}$ = 9.2, $^{4}J_{P^2OCCC^7}$ = 2.2, $^{2}J_{HC^8C^7}$ = 1.0, C-7), 120.3 ddddd (d) ($^{1}J_{HC^8}$ = 164.9, $^{3}J_{HC^6CC^8}$ = 7.7, $^{2}J_{HC^7C^8}$ = 1.4, $^{4}J_{HC^5CCC^8}$ = 1.3, C-8), 155.4 ddddd (d) ($^{3}J_{HC^7CC^{8a}}$ = 11.0, $^{3}J_{HC^5CC^{8a}}$ = 8.3, $^{2}J_{P^2OC^{8a}}$ = 7.3, $^{2}J_{HC^8C^{8a}}$ = 3.4, $^{4}J_{HC^5CCC^{8a}}$ = 1.4, C-8a), 148.5 ddq (dd) ($^{1}J_{P^{3b}C^{4b}}$ = 63.5, $^{1}J_{P^2C^{8b}}$ = 56.1, $^{3}J_{HC^{12b}CC^{4b}}$ = 2.8, C-4b), 158.4 ddq (dd) ($^{2}J_{P^{3b}CC^{5b}}$ = 23.8, $^{2}J_{P^2CC^{5b}}$ = 5.5, $^{2}J_{HC^{12b}C^{5b}}$ = 6.4, C-5b), 143.0 dttdd (dd), ($^{2}J_{P^{3b}NC^{6b}}$ = 10.7, $^{3}J_{HC^{8b,10b}CC^{6b}}$ = 8.7, $^{2}J_{HC^{7b,11b}C^{6b}}$ = 1.7-2.0, $^{4}J_{HC^{9b}CCC^{6b}}$ = 1.0-1.3, $^{4}J_{P^2CP^{3b}NC^{6b}}$ = 0.8, C-6b), 120.6 ddm (d) (C-11b, $^{1}J_{HC^{7b,11b}}$ = 161.4, $^{3}J_{P^{3b}NCC^{7b,11b}}$ = 9.5, $^{3}J_{HC^{11b}CC^{7b}}$ = 7.5-8.5, $^{3}J_{HC^{7b}CC^{11b}}$ = 7.5-8.5, $^{2}J_{HC^{8b,10b}C^{7b,11b}}$ = 2.2, $^{4}J_{HC^{9b}CCC^{7b,11b}}$ = 1.3, C-7b), 129.6 ddd (s) (C-10b, $^{1}J_{HC^{8b,10b}}$ = 161.0, $^{3}J_{HC^{8b}CC^{10b}}$ = 7.6-7.7, $^{3}J_{HC^{10b}CC^{8b}}$ = 8.6, $^{2}J_{HC^{9b}C^{10b}}$ = 1.1,

C-8b), 127.8 dtdd (d) ($^{1}J_{HC^{9b}}$ = 162.5, $^{3}J_{HC^{7b,11b}CC^{9b}}$ 8.8, $^{5}J_{P^{3b}NCCCC^{9b}}$ = 1.7, $^{2}J_{HC^{10b}C^{9b}}$ = 1.0, C-9b), 15.4 qdd (dd) ($^{1}J_{HC^{12b}}$ = 128.8, $^{3}J_{P^{3b}CCC^{12b}}$ = 8.4, $^{3}J_{P^{2}CCC^{12b}}$ = 1.0, C-12b). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 238.5 (br. d, $^{2}J_{P^{2}CP^{3b}}$ = 16.6, P-3b), 156.3 (d, $^{2}J_{P^{3b}CP^{2}}$ = 16.6, P-2). IR (KBr pellet): ν = 3440, 3100, 3066, 3027, 3012, 2958, 2914, 1734, 1664, 1606, 1579, 1492, 1475, 1457, 1424, 1383, 1346, 1286, 1227, 1206, 1153, 1129, 1070, 1043, 1014, 960, 930, 904, 880, 869, 787, 767, 754, 748, 686, 656, 632, 586, 543, 527, 496, 473 cm^{-1}. MS: *m/z* (%) = 342 [$(M)^{+\bullet}$, 61]. Anal. Calcd. for **1** ($C_{16}H_{12}N_2O_3P_2$) (342.22): C, 56.15; H, 3.53; N, 8.19; P, 18.10. Found: C, 56.03; H, 3.73; N, 8.14; P, 17.96 %.

***2-(5-Methyl-2-phenyl-2H-1,2,3-diazaphosphol-4-yl)-2,5-dioxo-4,4-bis(ethoxycarbonyl)-benzo[f]-1,3,2-dioxaphosphepine* (2)**

Mesoxalic acid diethyl ester (0.87 g, 0.005 mol) was added to a solution of compound **1** (1.71 g, 0.005 mol) in CH_2Cl_2 (10 mL) at –10 °C. The reaction mixture was kept for 1 day. Then the solvent was removed *in vacuo* (0.1 Torr) and a light-yellow oil was obtained. The oil was washed with a mixture of CH_2Cl_2 / hexane and dried *in vacuo* (0.1 Torr) to afford 2.28 g (89 %) of **2**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (dd, $^{3}J_{HCCH}$ = 7.9, $^{4}J_{HCCCH}$ = 1.7, 1H, H-6), 7.68 (d, $^{3}J_{HCCH}$ = 8.2, 1H, H-7b), 7.59 (ddd, $^{3}J_{HCCH}$ = 7.4, $^{3}J_{HCCH}$ = 8.0, $^{4}J_{HCCCH}$ = 0.8, 1H, H-8), 7.38 (dd, $^{3}J_{HCCH}$ = 8.1, $^{3}J_{HCCH}$ = 7.3, 1H, H-8b), 7.27-7.32 (m, 2H, H-9b, H-7b), 7.10 (ddd, $^{3}J_{HCCH}$ = 8.2, $^{4}J_{P^{2}OCCH}$ =1.2, $^{4}J_{HCCCH}$ =1.2, 1H, H-9), 4.41 (q, $^{3}J_{HCCH}$ = 7.1, 2H, CH_2), 4.27 (m, *A*- and *B*-parts of ABX_3 system, $^{3}J_{H_AH_B}$ = 12.0, $^{3}J_{HCCH}$ = 7.1, CH_AH_B), 2.71 (s, 1H, H-12b), 1.33 (t, $^{3}J_{HCCH}$ = 7.1, 3H, H-12), 1.18 (t, $^{3}J_{HCCH}$ = 7.1, 3H, H-15). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 88.6 d (d)

($^{2}J_{P^{2}OC^{4}}$ = 8.3, C-4), 185.3 d (s), ($^{3}J_{HC^{6}CC^{5}}$ = 3.3, C-5), 125.9 m (d) ($^{3}J_{P^{2}OCC^{5a}}$ = 1.8, C-5a), 131.8 br. ddd (d) ($^{1}J_{HC^{6}}$ = 166.3, $^{3}J_{HC^{8}CC^{6}}$ = 8.4, $^{5}J_{P^{2}OCCCC^{6}}$ = 1.4, C-6), 126.6 ddd (d) ($^{1}J_{HC^{7}}$ = 164.4, $^{3}J_{HC^{9}CC^{7}}$ = 8.2, $^{5}J_{P^{2}OCCCC^{7}}$ = 1.0, C-7), 137.0 (dddd (s) ($^{1}J_{HC^{8}}$ = 164.1, $^{3}J_{HC^{6}CC^{8}}$ = 8.9, $^{2}J_{HC^{9}C^{8}}$ = 2.0, $^{2}J_{HC^{7}C^{8}}$ = 1.2, C-8), 122.3 dddd (d) ($^{1}J_{HC^{9}}$ = 159.8, $^{3}J_{P^{2}OCC^{9}}$ = 5.7, $^{2}J_{HC^{8}C^{9}}$ = 2.3, $^{4}J_{HC^{6}CCC^{9}}$ = 1.0, C-9), 149.2 dddd (s) ($^{2}J_{P^{2}OC^{9a}}$ = 8.4, $^{3}J_{HC^{8}CC^{9a}}$ = 7.0, $^{3}J_{HC^{6}CC^{9a}}$ = 5.2, $^{2}J_{HC^{9}C^{9a}}$ = 2.3, C-9a), 163.0 dt (d) ($^{3}J_{P^{2}OCC^{10}}$ = 7.4, $^{3}J_{HC^{11}CC^{10}}$ = 3.4, C-10), 162.0 dt (d) ($^{3}J_{P^{2}OCC^{13}}$ = 8.3, $^{3}J_{HC^{14}CC^{13}}$ = 3.4, C-13), 63.7 tq (s) ($^{1}J_{HC^{11}}$ = 149.5, $^{2}J_{HC^{12}C^{11}}$ = 4.4, C-11), 63.5 tq (s) ($^{1}J_{HC^{14}}$ = 149.5, $^{2}J_{HC^{15}C^{14}}$ = 4.4, C-14), 13.8 qt (s) ($^{1}J_{HC^{12}}$ = 127.4, $^{2}J_{HC^{11}C^{12}}$ = 2.6, C-12), 13.7 qt (s) ($^{1}J_{HC^{15}}$ = 127.7, $^{2}J_{HC^{14}C^{15}}$ = 2.6, C-15), 132.1 ddq (dd) ($^{1}J_{P^{3b}C^{4b}}$ = 199.2, $^{1}J_{P^{2}C^{4b}}$ = 50.3, $^{3}J_{HC^{12b}CC^{4b}}$ = 2.8, C-4b), 158.9 ddq (dd) ($^{2}J_{P^{3b}CC^{5b}}$ = 11.0, $^{2}J_{P^{2}CC^{5b}}$ = 5.0, $^{2}J_{HC^{12b}C^{5b}}$ = 6.6, C-5b), 142.6 td (d) ($^{2}J_{P^{3b}NC^{6b}}$ = 9.0, $^{3}J_{HC^{8b,10b}CC^{6b}}$ = 7.9-8.5, $^{2}J_{HC^{7b,11b}C^{6b}}$ = 2.8, C-6b), 120.6 ddm (d) ($^{1}J_{HC^{7b}}$ = 162.2, $^{3}J_{P^{3b}NCC^{7b}}$ = 9.7, $^{3}J_{HC^{11b}CC^{7b}}$ = 7.9, $^{3}J_{HC^{9b}CC^{7b}}$ = 7.9-8.1, $^{2}J_{HC^{8b}C^{7b}}$ = 1.4, C-7b), 129.5 ddd (s) ($^{1}J_{HC^{8b}}$ = 162.3, $^{3}J_{HC^{10b}CC^{8b}}$ = 8.1, $^{2}J_{HC^{9b}C^{8b}}$ = 1.1, C-8b), 128.1 dt (s) ($^{1}J_{HC^{9b}}$ = 161.4, $^{3}J_{HC^{7b,11b}CC^{9b}}$ = 7.5, C-9b), 15.6 q (s) ($^{1}J_{HC^{12b}}$ = 129.6, C-12b). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 251.3 (br. d, $^{2}J_{P^{2}CP^{3b}}$ = 76.3, P-3b), 14.9 (d, $^{2}J_{P^{3b}CP^{2}}$ = 76.3, P-2). IR (film): ν = 3412, 3119, 3058, 2985, 2940, 2874, 2696, 1752, 1690, 1603, 1562, 1545, 1494, 1477, 1452, 1388, 1370, 1268, 1239, 1207, 1156, 1113, 1076, 1056, 1021, 925, 851, 831, 781, 738, 703, 628, 584, 557, 512 cm^{-1}. MS: *m/z* (%) = 516 [$(M)^{+\bullet}$, 0.3], 487 [M – C_2H_4, 0.1], 470 [M – OEt + H, 18], 424 [M – 2 C_2H_4, 3], 398 [M – $C(C(O)OEt)_2$, 3], 313 [M – $C(C(O)OEt)_2$ – C(O), 40], 121 [$C_6H_4OHC(O)$, 41], 92 [C_6H_4O, 24], 77 [C_6H_5, 36]. Anal. Calcd. for **2** ($C_{23}H_{22}N_2O_8P_2$) (516.38): C, 53.50; H, 4.29; N, 5.42; P, 12.00. Found: C, 53.21; H, 4.33; N, 5.22; P, 12.07 %.

2-(5-Methyl-2-phenyl-2H-1,2,3-diazaphosphol-4-yl)-2,5-dioxo-4-trifluoromethyl-4-ethoxycarbonylbenzo[f]-1,3,2-dioxaphosphepine **(3)**

Ethyltrifluoropyruvate (2.21 g, 0.013 mol) was added to a solution of compound **1** (4.44 g, 0.013 mol) and diethyl ether (15 mL) at –5 °C under argon atmosphere. The reaction mixture was allowed to reach 20 °C during 30 min and then it was kept at room temperature for one day. The solvent was removed *in vacuo* (0.1 Torr), the residue was washed with hexane and was dried *in vacuo* (0.1 Torr). Compound **3**, light-yellow oil, yield 5.32 g (80 %). It gradually crystallizes during 2 months under an inert atmosphere, m.p. 72-75 °C (mixture of diastereoisomers d_1 and d_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (dd, $^3J_{HCCH}$ = 7.9, $^4J_{HCCCH}$ = 1.7, 1H, H-6), 7.91 (dd, $^3J_{HCCH}$ = 7.9, $^4J_{HCCCH}$ = 1.7, 1H, H-6), 7.71 (br. d, $^3J_{HCCH}$ = 8.2, 1H, H-7), 7.56 (br. d, $^3J_{HCCH}$ = 8.2, 1H, H-7), 7.62 (br. ddd, $^3J_{HCCH}$ = 8.2, $^3J_{HCCH}$ = 7.9, $^4J_{HCCCH}$ = 1.4, 1H, H-8), 7.51 (br. ddd, $^3J_{HCCH}$ = 8.2, $^3J_{HCCH}$ = 7.9, $^4J_{HCCCH}$ = 1.7, 1H, H-8), 7.36 and 7.34 (m, H-8b), 7.30-7.35 (m, H-7b, H-9b), 7.02 and 7.28 (br. d, $^3J_{HCCH}$ = 8.2, H-9), 4.43 (m, *AB*-part of ABX_3-system, $^2J_{AB}$ = 10.7, $^3J_{HCCH}$ = 7.2, 2H, OCH_2), 4.19 and 4.06 (m, *AB*-part of ABX_3-system, $^2J_{AB}$ = 10.7, $^3J_{HCCH}$ = 7.2, 2H, OCH_AH_B), 2.76 (s, 3H, H-12b), 2.63 (s, 3H, H-12b), 1.32 (t, $^3J_{HCCH}$ = 7.2, 3H, $OCCH_3$), 1.11 (t, $^3J_{HCCH}$ = 7.2, 3H, $OCCH_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 84.6 qd (qd) ($^2J_{P^2OC}$ = 7.2, $^2J_{FCC}$ = 28.9, C-4), 84.9 qd (qd) ($^2J_{P^2OC}$ = 7.3, $^2J_{FCC}$ = 28.9, C-4), 185.6 dd (s) ($^3J_{HC^6CC^5}$ = 4.3, $^4J_{HC^7CCC^5}$ = 1.5, C-5), 182.4 br. d (s) ($^3J_{HC^6CC^5}$ = 4.0, C-5); 125.9 br. m (br. s) (C-5a), 126.7 br. m (br. s) (C-5a), 131.8 dd (s), ($^1J_{HC^6}$ = 166.4, $^3J_{HC^8CC^6}$ = 8.6, C-6), 131.6 dd (s) ($^1J_{HC^6}$ = 166.8, $^3J_{HC^8CC^6}$ = 8.2, C-6), 126.7 dd (s) ($^1J_{HC^7}$ = 165.4, $^3J_{HC^9CC^7}$ = 7.7, C-7), 126.6 dd (s), ($^1J_{HC^7}$ =

164.9, $^{3}J_{HC^{9}CC^{7}}$ = 7.6, C-7), 137.9 dd (s) ($^{1}J_{HC^{8}}$ = 163.5, $^{3}J_{HC^{6}CC^{8}}$ = 8.8, $^{2}J_{HCC^{8}}$ = 1.3, C-8), 136.8 br. ddd (s) ($^{1}J_{HC^{8}}$ = 161.6, $^{3}J_{HC^{6}CC^{8}}$ = 8.8, $^{2}J_{HCC^{8}}$ = 2.3, C-8), 121.9 dm (d) ($^{1}J_{HC^{9}}$ = 160.0-162.0, $^{3}J_{POCC^{9}}$ = 6.1, C-9), 121.88 dm (d) ($^{1}J_{HC^{9}}$ = 160.0-162.0, $^{3}J_{POCC^{9}}$ = 6.3, C-9), 148.6 ddddd (d) ($^{3}J_{HCCC^{9a}}$ = 10.5, $^{3}J_{HCCC^{9a}}$ = 9.0, $^{2}J_{P^{2}OC^{9a}}$ = 8.4, $^{2}J_{HC^{9}C^{9a}}$ = 3.9, $^{4}J_{HC^{7}CCC^{9a}}$ = 1.7, C-9a), 147.9 ddddd (d) ($^{3}J_{HCCC^{9a}}$ = 10.5, $^{3}J_{HCCC^{9a}}$ = 9.1, $^{2}J_{POC^{9a}}$ = 8.4, $^{2}J_{HC^{9}C^{9a}}$ = 4.0, $^{4}J_{HC^{7}CCC^{9a}}$ = 1.7, C-9a), 120.7 qd (qd) ($^{1}J_{FC^{10}}$ = 286.5, $^{2}J_{POC^{10}}$ = 13.1, C-10), 121.3 br.q (br.q) ($^{1}J_{FC^{10}}$ = 285.5, C-10), 161.1 dt (d) ($^{3}J_{HC^{12}OC^{11}}$ = 3.4-3.5, $^{3}J_{POCC^{11}}$ = 1.4, C-11), 160.7 dt (d) ($^{3}J_{POCC^{11}}$ = 3.5, $^{3}J_{HC^{12}OC^{11}}$ = 3.5, C-11), 64.6 tq (s) ($^{1}J_{HC^{12}}$ = 150.1, $^{2}J_{HC^{13}C^{12}}$ = 4.5, C-12), 64.2 tq (s) ($^{1}J_{HC^{12}}$ = 150.2, $^{2}J_{HC^{13}C^{12}}$ = 4.5, C-12), 13.4 qt (s) ($^{1}J_{HC^{13}}$ = 127.9, $^{2}J_{HC^{12}C^{13}}$ = 2.6, C-13); 13.2 qt (s) ($^{1}J_{HC^{13}}$ = 127.9, $^{2}J_{HC^{12}C^{13}}$ = 2.6, C-13), 131.3 ddq (dd) ($^{1}J_{P^{3b}C^{4b}}$ = 205.3, $^{1}J_{P^{2}C^{4b}}$ = 49.9, $^{3}J_{HC^{12b}CC^{4b}}$ = 2.8, C-4b), 130.7 ddq (dd) ($^{1}J_{P^{3b}C^{4b}}$ = 197.6, $^{1}J_{P^{2}C^{4b}}$ = 49.1, $^{3}J_{HC^{12b}CC^{4b}}$ = 2.8, C-4b), 159.0 dqd (dd) ($^{2}J_{P^{3b}CC^{5b}}$ = 11.2, $^{2}J_{HC^{12b}C^{5b}}$ = 6.5-6.6, $^{2}J_{P^{2}CC^{5b}}$ = 4.5, C-5b), 158.5 dqd (dd) ($^{2}J_{P^{3b}CC^{5b}}$ = 10.8, $^{2}J_{HC^{12b}C^{5b}}$ = 6.4-6.5, $^{2}J_{P^{2}CC^{5b}}$ = 4.2, C-5b), 142.4 br. dt (d) ($^{2}J_{PNC^{6b}}$ = 11.0, $^{3}J_{HC^{8b}CC^{6b}}$ = 8.9, C-6b), 142.1 br. dt (d) ($^{2}J_{PNC^{6b}}$ = 10.9, $^{3}J_{HC^{8b}CC^{6b}}$ = 8.9, C-6b), 120.4 dm (d) ($^{1}J_{HC^{7b}}$ = 162.0, $^{3}J_{PNCC^{7b}}$ = 9.7, C-7b), 120.1 dm (d) ($^{1}J_{HC^{7b}}$ = 162.0, $^{3}J_{PNCC^{7b}}$ = 9.7, C-7b), 129.4 dd (s) ($^{1}J_{HC^{8b}}$ = 161.9, $^{3}J_{HCCC^{8b}}$ = 7.7, C-8b), 129.3 dd (s) ($^{1}J_{HC^{8b}}$ = 162.0, $^{3}J_{HCCC^{8b}}$ = 7.7, C-8b), 128.1 br. dt (s) ($^{1}J_{HC^{9b}}$ = 163.3, $^{3}J_{HC^{7b}CC^{9b}}$ = 7.6, C-9b), 128.0 br. dt (s) ($^{1}J_{HC^{9b}}$ = 163.3, $^{3}J_{HC^{7b}CC^{9b}}$ = 7.6, C-9b), 15.3 br. qd (br. d) ($^{1}J_{HC^{10b}}$ = 129.7, $^{3}J_{P^{3b}CCC^{10b}}$ = 3.5, C-12b). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 252.1 (br. d, $^{2}J_{PCP}$ = 74.1, P-3b), 250.1 (br. d, $^{2}J_{PCP}$ = 82.3, P-3b), 16.1 (d, $^{2}J_{PCP}$ = 82.3, P-2), 12.4 (d, $^{2}J_{PCP}$ = 74.1, P-2). IR (film): ν = 3056, 2986, 2941, 2835, 2694, 1770, 1705, 1603, 1493, 1428, 1451, 1387, 1371, 1282, 1224, 1156, 1141, 1069, 1025, 925, 846, 739, 704, 691, 673, 652, 640, 618 cm^{-1}.

MS: *m/z* (%) = 512 [$(M)^{+\bullet}$, 2], 484 [M – C_2H_4, 51], 466 [M – OEt – H, 5], 439 [M – C(O)OEt – H, 1], 421 [M – C(O)OEt – F + H, 1], 403 [M – C(O)OEt – 2F + 2H, 1], 382 [M – C(O)OEt – 3F + 2H, 0.2], 238 [$C_9H_8N_2O_2P_2$, 6], 222 [$C_9H_8N_2OP_2$, 10], 178 [$C_8H_3O_3P$, 10], 121 [$C_7H_4O_2$ + H, 40], 77 [C_6H_5, 100]. Anal. Calcd. for **3** ($C_{21}H_{17}F_3N_2O_6P_2$) (512.31): C, 49.23; H, 3.34; N, 5.47; P, 12.09. Found: C, 49.34; H, 3.41; N, 5.39; P, 12.11 %.

***2-(5-Methyl-2-phenyl-2H-1,2,3-diazaphosphol-4-yl)-2,5-dioxo-4,4-bis(trifluoromethyl)-benzo[f]-1,3,2-dioxaphosphepine* 5**

Hexafluoroacetone (1.99 g, 0.012 mol) was condensed into a solution of compound **1** (4.0 g, 0.012 mol) dissolved in a mixture of CCl_4 / CH_2Cl_2 (20 mL, 1 : 1) at –40 °C. The reaction mixture was slowly (8-10 h) warmed up to 20 °C and kept at that temperature for one day. The colourless crystals of compound **5** formed were filtered off, washed with CCl_4 / CH_2Cl_2-mixture and dried *in vacuo* (0.1 Torr). Yield 5.54 g, 93 %, m.p. 173-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, $^3J_{H^7CCH^6}$ = 7.9, $^4J_{H^8CCCH^6}$ = 1.6, 1H, H-6), 7.77 (m, $^3J_{H^{8b}CCH^{7b}}$ = 7.8, 2H, H-7b), 7.64 (dddd, $^3J_{H^9CCH^8}$ = 8.2, $^3J_{H^7CCH^8}$ = 7.4, $^4J_{H^6CCCH^8}$ = 1.6, $^5J_{P^2OCCCH^8}$ = 1.1, 1H, H-8), 7.47 (m, $^3J_{H^{7b}CCH^{8b}}$ = 7.7, $^3J_{H^{9b}CCH^{8b}}$ = 7.4, 2H, H-8b), 7.40 (br. m, $^3J_{H^{8b}CCH^{9b}}$ = 7.4, 1H, H-9b), 7.38 (br. m, $^3J_{H^6CCH^7}$ = 7.9-8.0 Hz, $^3J_{H^8CCH^7}$ = 7.4, 1H, H-7), 7.08 (br. d, $^3J_{H^8CCH^9}$ = 8.2, 1H, H-9), 2.76 (s, 3H, H-12b). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 83.6 sept.d (sept.d) ($^2J_{FCC^4}$ = 30.3, $^2J_{P^2OC^4}$ = 7.6, C-4), 185.5 ddd (d) ($^3J_{HC^6CC^5}$ = 4.3, $^3J_{P^2OCC^5}$ = 1.9, $^4J_{HCCCC^5}$ = 1.7, C-5), 128.0 br.m (br.s) (C-5a). 132.4 ddddd (d) ($^1J_{HC^6}$ = 166.4, $^3J_{HC^8CC^6}$ = 8.3, $^2J_{HC^7C^6}$ = 2.6, $^4J_{P^2OCCC^6}$ = 1.2, $^4J_{HC^9CCC^6}$ = 1.2, C-6), 126.5 dddd (d) ($^1J_{HC^7}$ = 165.2, $^3J_{HC^9CC^7}$ = 8.1, $^2J_{HC^8C^7}$ = 1.1, $^4J_{P^2OCCC^7}$ = 1.1, C-7),

136.8 ddd (s) ($^{1}J_{HC^{8}}$ 163.3, $^{3}J_{HC^{6}CC^{8}}$ = 9.0, $^{2}J_{HC^{9}C^{8}}$ = 2.1, C-8), 121.7 ddddd (d) ($^{1}J_{HC^{9}}$ = 165.8, $^{3}J_{P^{2}OCC^{9}}$ = 8.1, $^{3}J_{HC^{7}CC^{9}}$ = 8.0, $^{2}J_{HC^{8}C^{9}}$ = 1.2, $^{4}J_{HC^{6}CCC^{9}}$ = 1.2, C-9), 148.0 ddddd (d) ($^{3}J_{HC^{8}CC^{9a}}$ = 10.4, $^{3}J_{HC^{6}CC^{9a}}$ = 9.0, $^{2}J_{P^{2}OC^{9a}}$ = 8.2, $^{2}J_{HC^{9}C^{9a}}$ = 4.1, $^{4}J_{HC^{7}CCC^{9a}}$ = 1.7, C-9a), 120.1 qdq (qdq) ($^{1}J_{FC^{10}}$ = 288.3, $^{3}J_{P^{2}OCC^{10}}$ = 3.0, $^{4}J_{FC^{11}CC^{10}}$ = 1.1, C-10), 120.0 qdq (qdq) ($^{1}J_{FC^{11}}$ = 290.0, $^{3}J_{P^{2}OCC^{11}}$ = 10.0, $^{4}J_{FC^{10}CC^{11}}$ = 1.3, C-11), 130.1 ddq (dd) ($^{1}J_{P^{3b}C^{4b}}$ = 204.9, $^{1}J_{P^{2}C^{4b}}$ = 49.0, $^{3}J_{HC^{12b}CC^{4b}}$ = 2.8, C-4b), 159.2 ddq (dd) ($^{2}J_{P^{3b}CC^{5b}}$ = 10.5, $^{2}J_{P^{2}CC^{5b}}$ = 4.4, $^{2}J_{HC^{12b}C^{5b}}$ = 4.2, C-5b), 142.7 dtt (d) ($^{2}J_{P^{3b}NC^{6b}}$ = 11.1, $^{3}J_{HC^{8b}CC^{6b}}$ = 8.5-9.0, $^{2}J_{HC^{7b}C^{6b}}$ = 2.7, C-6b), 120.9 dm (d) ($^{1}J_{HC^{7b}}$ = 162.2, $^{3}J_{P^{3b}NCC^{7b}}$ = 9.6, $^{3}J_{HC^{7b}CC^{7b}}$ = 6.5-7.5, $^{3}J_{HC^{9b}CC^{7b}}$ = 7.0, C-7b), 129.8 ddd (s) ($^{1}J_{HC^{8b}}$ = 162.6, $^{3}J_{HC^{8b}CC^{8b}}$ = 7.5, $^{2}J_{HCC^{8b}}$ = 1.2, C-8b), 128.7 dtd (d) ($^{1}J_{HC^{9b}}$ = 162.5, $^{3}J_{HC^{7b}CC^{9b}}$ = 7.6, $^{5}J_{P^{3b}NCCCC^{9b}}$ = 1.6, C-9b), 15.6 q (s) ($^{1}J_{HC}$ = 129.6, C-10b). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 253.2 (br. d, $^{2}J_{P^{2}CP^{3b}}$ = 82.8, P-3b), 15.8 (d, $^{2}J_{P^{3b}CP^{2}}$ = 82.8, P-2). IR (KBr pellet): ν = 3436, 3103, 3035, 2998, 2926, 2853, 1708, 1693, 1602, 1573, 1493, 1481, 1448, 1427, 1383, 1357, 1277, 1247, 1234, 1210, 1173, 1151, 1124, 1066, 1036, 1020, 980, 945, 931, 891, 878, 849, 786, 767, 754, 739, 712, 677, 651, 602, 579, 565, 543, 517, 500, 481, 457 cm^{-1}. MS: *m/z* (%) = 481 [MH – CO, 100]$^{+}$. Anal. Calcd. for **5** ($C_{19}H_{12}F_6N_2O_4P_2$) (508.25): C, 44.90; H, 2.38; N, 5.51; P, 12.19. Found: C, 44.95; H, 2.39; N, 5.47; P, 12.07 %.

***2-(5-Methyl-2-phenyl-2H-1,2,3-diazaphosphol-4-yl)-2,5-dioxo-4-trichloromethyl)-benzo[f]-1,4,2-dioxaphosphepine* 7**

A mixture of compound **1** (2.74 g, 0.008 mol), CH_2Cl_2 (10 mL), diethyl ether (10 mL), and chloral (1.18 g, 0.008 mol) was kept for 5 days. A crystalline precipitate was gradually

formed. Filtration and washing with hexane followed by drying *in vacuo* (0.1 Torr) afforded 0.32 g (9 %) of compound **7** (d_1, d_2) as colorless crystals, m.p. 165-171 °C. After recrystallization from CH_2Cl_2 was obtained 0.18 g (5 %) of compound **7** (d_1), m.p. 169-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$, d_1): δ = 5.11 (d, $^2J_{PCH3}$ = 2.8, H-3), 8.02 (dd, $^3J_{H7CCH6}$ = 7.8, $^4J_{H8CCCH6}$ = 1.8, H-6), 7.40 (m, H-9b, H-7), 7.75 (m, H-7b), 7.68 (dddd, $^3J_{H9CCH8}$ = 8.3, $^3J_{H7CCH8}$ = 7.4-7.5, $^4J_{H6CCCH8}$ = 1.8, $^5J_{POCCCH8}$ = 1.0, H-8), 7.45 (m, H-8b), 7.07 (ddd, $^3J_{H8CCH9}$ = 8.3, $^4J_{H7CCCH9}$ = 1.2, $^4J_{POCCH9}$ = 1.0, H-9), 2.82 (s, H-12b). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 86.0 ddd (dd) ($^1J_{HC3}$ = 146.2, $^1J_{PC3}$ = 104.5, $^3J_{P^{II}CPC3}$ = 2.9, C-3), 163.7 br. d (br s) ($^3J_{HC6CC5}$ = 6.0, C-5), 126.4 m (d) ($^3J_{POCC5a}$ = 6.2, C-5a), 133.9 br. dd (d) ($^1J_{HC6}$ = 166.3, $^3J_{HC8CC6}$ = 8.7, C-6), 127.6 br. dd (d) ($^1J_{HC7}$ = 166.0, $^3J_{HC9CC7}$ = 7.8, $^5J_{POCCCC7}$ = 1.7, C-7), 136.1 br. ddd (d) ($^1J_{HC8}$ = 165.6, $^3J_{HC6CC8}$ = 8.4, $^2J_{HC9C8}$ = 1.3, $^4J_{POCCC8}$ = 1.0, C-8), 123.7 br. ddd (d) ($^1J_{HC9}$ = 165.0-166.0, $^3J_{HC7CC9}$ = 8.5, $^3J_{POCC9}$ = 3.9, C-9), 93.5 dd (d) ($^2J_{PC3C10}$ = 6.5, $^2J_{HC3C10}$ = 6.5, C-10), 133.0 ddq (dd) ($^1J_{P3bC4b}$ = 201.6, $^1J_{P2C4b}$ = 48.6, $^3J_{HC12bCC4b}$ = 3.5, C-4b), 159.7 m (dd) ($^2J_{P3bCC5b}$ = 7.8, $^3J_{P2CC5b}$ = 4.3, C-5b), 142.6 m (d) ($^1J_{P^{II}NC6b}$ = 11.1, C-6b), 120.8 ddm (d) ($^1J_{HC7b}$ = 161.1, $^3J_{P3bNCC7b}$ = 9.8, C-7b), 129.9 dd (s) ($^1J_{HC8b}$ = 161.8, $^3J_{HC8b'CC8b}$ = 8.0, C-8b), 128.8 br. dt (d) ($^1J_{HC9b}$ = 162.6, $^3J_{HC7bCC9b}$ = 7.8, $^5J_{P3bNCCCC9b}$ = 1.5, C-9b), 16.6 q (s) ($^1J_{HC10b}$ = 130.0, C-12b). ^{31}P NMR (36.46 MHz, $CDCl_3$): δ = 251.9 (br. d, $^2J_{P2CP3b}$ = 84.5, P-3b), 11.3 (d, $^2J_{P3bCP2}$ = 84.5, P^2). IR (KBr pellet): ν = 3421, 3411, 3397, 2884, 1741, 1602, 1591, 1578, 1490, 1478, 1454, 1430, 1382, 1343, 1288, 1266, 1254, 1236, 1214, 1158, 1133, 1112, 1080, 1057, 1040, 1015, 953, 931, 911, 872, 846, 808, 783, 772, 755, 743, 706, 689, 666, 639, 606, 585, 549, 521, 509 cm^{-1}. Anal. Calcd. for **7**

($C_{18}H_{13}Cl_3N_2O_4P_2$) (489.61): C, 44.16; H, 2.68; Cl, 21.72; N, 5.72; P, 12.65. Found: C, 43.92; H, 2.74; Cl, 21.33; N, 5.57; P, 12.44 %.

After separation of precipitate **7**, the filtrate was dried *in vacuo* (0.1 Torr) and 3.43 g (88 %) of 2-chlorocarbonylphenoxy-2,2-dichlorovinyloxy-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)phosphonate **6** was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (br. d, *X*-part of *ABMX*-system, $^3J_{H^7CCH^6}$ = 8.0, 1H, H-6), 7.77 (br. d, *XX'*-part of *ABB'XX'*-system, $^3J_{H^{8b}CCH^{7b}}$ = 8.0, 2H, H-7b), 7.71 (br. dd, *B*-part of *ABMX*-system, $^3J_{H^9CCH^8}$ = 8.4, $^3J_{H^7CCH^8}$ = 7.7, 1H, H-8), 7.55 (br. d, *A*-part *ABMX*-system, $^3J_{H^8CCH^9}$ = 8.3, 1H, H-9), 7.44 (br. dd, $^3J_{H^{9b}CCH^{8b}}$ = 8.1, $^3J_{H^{7b}CCH^{8b}}$ = 7.9, 2H, H-8b), 7.36 (br. dd, *M*-part *ABMX*-system, $^3J_{H^8CCH^7}$ = 7.6, $^3J_{H^6CCH^7}$ = 8.0, 1H, H-7), 7.35 (br. t, *A*-part of *ABB'XX'*-system, $^3J_{H^{8b}CCH^{9b}}$ = 8.1, 1H, H-9b), 7.21 (d, $^3J_{POCH}$ 6.6, 1H, OCH=), 2.75 (s, 3H, H-12b). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 148.3 ddddd (d) ($^3J_{HC^8CC^{9a}}$ = 10.7, $^3J_{HC^6CC^{9a}}$ = 9.0, $^2J_{POC^{9a}}$ = 8.3, $^2J_{HC^9C^{9a}}$ = 3.2, $^4J_{HC^7CCC^{9a}}$ = 1.7, C-9a), 126.1 br. ddd (d) ($^3J_{HC^7CC^{5a}}$ = 8.0, $^3J_{POCC^{5a}}$ = 5.7, $^3J_{HC^9CC^{5a}}$ = 5.8, C-5a), 134.3 dddd (s) ($^1J_{HC^6}$ = 165.5, $^3J_{HC^8CC^6}$ = 8.5, $^2J_{HC^7C^6}$ = 2.2, C-6), 126.0 dddd (d) ($^1J_{HC^7}$ = 165.3, $^3J_{HC^9CC^7}$ = 7.8, $^5J_{P^2OCCCC^7}$ = 1.1, C-7), 136.1 ddd (d) ($^1J_{HC^8}$ = 164.0, $^3J_{HC^6CC^8}$ = 8.9, $^4J_{P^2OCCC^8}$ = 1.4, C-8), 122.3 ddd (d) ($^1J_{HC^9}$ = 159.4, $^3J_{HC^7CC^9}$ = 8.0, $^3J_{P^2OCC^9}$ = 3.3, C-9); 164.0 br. dd (s) ($^3J_{HC^6CC^5}$ = 6.7, $^4J_{HCCCC^5}$ = 1.2, C-5), 132.9 dd (d) ($^1J_{HC^4}$ = 201.1, $^2J_{P^2OC^4}$ = 4.5, C-4), 114.7 dd (d) ($^2J_{HCC^{10}}$ = 13.8, $^3J_{P^2OCC^{10}}$ = 13.8, C-10), 134.7 ddq (dd) ($^1J_{P^{3b}C^{4b}}$ = 201.8, $^1J_{P^2C^{4b}}$ = 48.7, $^3J_{HC^{12b}CC^{4b}}$ = 2.8, C-4b), 158.7 ddq (dd) ($^2J_{P^{3b}CC^{5b}}$ = 9.7, $^2J_{P^2CC^{5b}}$ = 4.8, $^2J_{HC^{12b}C^{5b}}$ = 4.7, C-5b), 142.7 br. dm (d) ($^2J_{P^{3b}NC^{6b}}$ = 11.1, $^3J_{HC^{8b}CC^{6b}}$ = 8.5, C-6b), 120.7 ddm (d) ($^1J_{HC^{7b}}$ = 162.2, $^3J_{P^{3b}NCC^{7b}}$ = 9.7, $^3J_{HC^{11b}CC^{7b}}$ = 6.0-8.0, $^3J_{HC^{9b}CC^{7b}}$ = 7.0, C-7b), 129.6 dd (s) ($^1J_{HC^{8b}}$ = 162.1, $^3J_{HC^{10b}CC^{8b}}$ = 8.1, C-

8b), 128.3 br. dtd (d) ($^{1}J_{HC^{9b}}$ = 162.2, $^{3}J_{HC^{7b}CC^{9b}}$ = 7.5, $^{5}J_{P^{3b}NCCCC^{9b}}$ = 1.1, C-9b), 15.6 q (s) ($^{1}J_{HC^{12b}}$ = 129.7, C-12b). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 251.9 (br. d, $^{2}J_{P^{2}CP^{3b}}$ = 84.5, P^{3b}), 11.3 (d, $^{2}J_{P^{3b}CP^{2}}$ = 84.5, P^{2}). IR (film): ν = 3107, 3076, 1774, 1708, 1599, 1496, 1478, 1450, 1384, 1342, 1282, 1214, 1195, 1151, 1133, 1073, 1025, 977, 926, 848, 815, 754, 737, 690, 661, 646, 613, 513 cm^{-1}. MS: *m/z* (%) = 488 [$(M)^{+\bullet}$, 1], 453 [M – Cl, 10], 418 [M – 2 Cl, 1], 406 [M – CCl_2, 3], 377 [M – OCH=CCl_2, 5], 358 [M – OCH=CCl_2 – Cl, 23], 330 [M – OCH=CCl_2 – C(O)Cl, 5], 176 [$C_9H_8N_2P$ + H, 88]$^{+}$, 92 [C_6H_5O, 92]. Anal. Calcd. for **6** ($C_{18}H_{13}Cl_3N_2O_4P_2$) (489.61): C, 44.16; H, 2.68; Cl, 21.72; N, 5.72; P, 12.65. Found: C, 43.87; H, 2.81; Cl, 21.51; N, 5.63; P, 12.57 %.

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Supporting information

Hydrogen bonds in the molecules of compounds **1**, **5**, **7** and figures of NMR spectra of compounds **1-3**, **5-7** are included in the Supplemental Materials (Figures S 1 – S 57).

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