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Pyridine and benzyltriethylammonium chloride *ate*-complexes of 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole in reactions with alk-1-ynes

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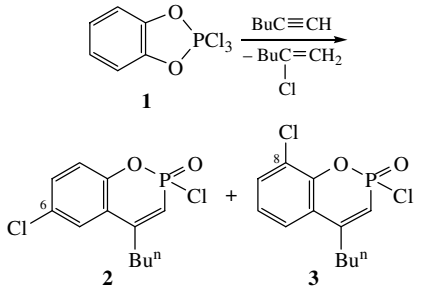
The reactions of the pyridine and benzyltriethylammonium chloride *ate*-complexes of 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole with alk-1-ynes afford 4-alkyl-2,6-dichloro- and 4-alkyl-2,7-dichloro-2-oxobenzo[*e*]-1,2-oxaphosphorinines; preferable chlorination of the phenylene moiety at the 7-position occurs when the *ate*-complex of 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole and benzyltriethylammonium chloride is used.

2,2,2-Trihalobenzo[*d*]-1,3,2-dioxaphospholes react with arylacetylenes to give phosphorus analogues of natural coumarin, *viz*., benzo[*e*]-1,2-oxaphosphorinines,[1,2] the derivatives of which exhibit activity against the protein tyrosine phosphatases and anticancer properties.[3,4] This reaction occurs under mild conditions and results in a phosphoryl group and a P–C bond formation, *ipso*-substitution of an oxygen atom in the phenylene moiety and preferential halogenation of the latter at the *para* position with respect to the endocyclic oxygen atom of the phosphorinine heterocycle. We found recently that alkylacetylenes also undergo a similar reaction.[5] 2,2,2-Trichlorobenzo[*d*]-1,3,2-dioxaphosphole **1** reacts with hex-1-yne to give two benzo[*e*]-1,2-phosphorinines **2** and **3** in a 10:1 ratio (Scheme 1).



Scheme 1

In this work, we have shown for the first time that the reaction with alkylacetylenes can also occur with anionic and neutral derivatives of hexacoordinate phosphorus, so-called *ate*-complexes **4** and **5** of dioxaphosphole **1** with pyridine (δ_P –129.7 and –137.1, CH_2Cl_2)[6] and benzyltriethylammonium chloride (δ_P –97.1, CH_2Cl_2).[7] The reactivity of hexacoordinate phosphorus derivatives has been studied insufficiently; they are usually considered as intermediates in the nucleophilic substitution at pentacoordinate phosphorus.[8–13] The reaction rate of compounds **4** or **5** with alk-1-ynes was considerably smaller and the process came to completion on keeping the reaction mixture for 20–30 days (20 °C). For example, the neutral phosphole–pyridine complex gives 2-chlorobenzo[*e*]-1,2-oxaphosphorinine derivative **2** (δ_P 16.7, $^2J_{PCH}$ 24.3 Hz) in 20–25 days in a high yield (~90%).[†] *ate*-Complex **4** dissolved during the reaction and a crystalline precipitate of pyridinium chloride was formed, which was then separated and identified spectroscopically. The formation of pyridinium chloride suggests that chlorination of the aromatic moiety occurs. The position of the chlorine atom at the phenylene ring was determined by a comparison of the ^{1}H and ^{13}C NMR spectra of the hydrolysis product, *viz*., phosphonic acid **6** (Scheme 2), with the spectra of compound **6** obtained previously.[5] However, the reaction also gives about 9% of isomer **3** as a by-product, which was isolated as stable hydroxy derivative **7** by fractional crystallization from acetone. The structures of this compound and its calcium salt **8** were confirmed by X-ray diffraction analysis (Figures 1 and 2, Table 1).[†,‡] Figure 1 shows two molecules of phosphorinine **7** forming a dimer due to an intermolecular hydrogen bond. The phosphorinine heterocycle has the conformation of a strongly depressed sofa, where the P(2) deviates by 0.155(1) Å from the C(2)C(3)C(4)C(5)C(6)C(7)C(8)O(1) moiety, which is planar to within 0.037(1) Å. The carbon atoms of the butyl substituent

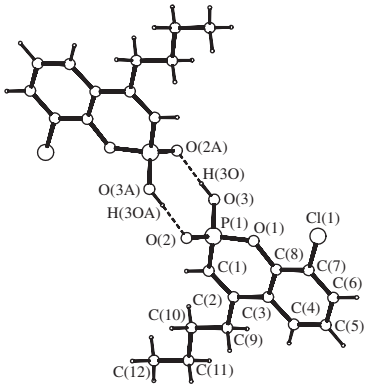


Figure 1 The H-bonded dimer of hydroxyphosphorinine **7**. Selected bond lengths (Å): Cl(1)–C(7) 1.7306(18), P(1)–O(2) 1.4847(14), P(1)–O(3) 1.5424(15), P(1)–O(1) 1.5985(14), P(1)–C(1) 1.7520(18), O(1)–C(8) 1.378(2), C(1)–C(2) 1.349(3), C(2)–C(3) 1.480(2), C(3)–C(8) 1.402(2); selected bond angles (°): O(2)–P(1)–O(3) 113.96(8), O(2)–P(1)–O(1) 110.93(8), O(3)–P(1)–O(1) 104.00(8), O(2)–P(1)–C(1) 113.75(9), O(3)–P(1)–C(1) 109.46(9), O(1)–P(1)–C(1) 103.84(8), C(8)–O(1)–P(1) 126.5(1), C(2)–C(1)–P(1) 123.4(1), C(1)–C(2)–C(3) 121.5(1). The atoms labeled with A are obtained from the basic ones by the symmetry operation (–*x*, –*y*, –*z* + 1).

are also located in the same plane. The exocyclic substituents O(2) and O(3) at the phosphorus atom deviate by –1.431(1) and 1.104(1) Å, respectively, from the planar moiety. The configuration of the calcium ion in a molecule of **8** is an octahedron

† The melting points are uncorrected; measurements involved a Boetius melting point apparatus. NMR spectra were recorded on Bruker Avance-600 (^{1}H, 600 MHz; ^{13}C, 150.9 MHz) and Bruker CXP-100 (^{31}P, 36.48 MHz) spectrometers. The δ_H and δ_P values were determined relative to an internal (HMDS) or external (H_3PO_4) standard. The δ_C values were determined relative to the signal of the deuterated solvent. The IR spectrum was recorded on a Bruker Vector-22 instrument in Nujol. The EI mass spectra were obtained on a TRACE MS Finnigan MAT instrument; the electron energy was 70 eV, the ion source temperature was 200 °C. The samples were introduced into the ion source using a direct inlet system. Heating of the evaporator tube was programmed from 35 to 150 °C at a rate of 35 K min^{-1}. The mass-spectrometric data were processed using the Xcalibur program.

Crystallographic data. Crystals of **7** ($C_{12}H_{14}ClO_3P$, M = 272.65) are triclinic, space group $P\bar{1}$, at 120 K: a = 8.7016(6), b = 8.8102(7) and c = 8.9494(7) Å, α = 108.9800(10)°, β = 101.0580(10)°, γ = 100.8420(10)°, V = 613.11(8) Å^3, Z = 2 (Z' = 1), d_{calc} = 1.477 g cm^{-3}, (MoKα) = 4.35 cm^{-1}, F(000) = 284. Intensities of 6388 reflections were measured with a Bruker SMART 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 56°$] and 2953 independent reflections [R_{int} = 0.0228] were used in further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined in the isotropic approximation. For **7** the refinement converged to wR_2 = 0.0991 and GOF = 1.004 for all independent reflections [R_1 = 0.0407 was calculated against F for 2386 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

Crystals of **8** ($C_{72}H_{86}CaCl_6O_{20}P_6$, M = 1707.99) are triclinic, space group $P\bar{1}$, at 120 K: a = 11.350(3), b = 13.317(4) and c = 13.850(4) Å, α = 97.415(7)°, β = 94.694(7)° and γ = 103.765(6)°, V = 2002.5(10) Å^3, Z = 1 (Z' = 1/2), d_{calc} = 1.416 g cm^{-3}, (MoKα) = 4.67 cm^{-1}, F(000) = 888. Intensities of 14426 reflections were measured with a Bruker SMART 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 54°$] and 8301 independent reflections [R_{int} = 0.0244] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atoms of OH groups and water molecules were located from a Fourier synthesis of electron density; the H(C) positions were calculated. All hydrogen atoms were refined in the isotropic approximation. For **8** the refinement converged to wR_2 = 0.1145 and GOF = 1.046 for all independent reflections [R_1 = 0.0481 was calculated against F for 5995 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

CCDC 658939 and 658940 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.

‡ *Reaction of 2,2,2-trichlorobenzo[*d*]-1,2,3-dioxaphosphole* ***1*** *with hex-1-yne in the presence of pyridine*. A solution of hex-1-yne (4.2 ml, 0.036 mol) in 15 ml of CH_2Cl_2 was added to *ate*-complex **4** (4.5 g, 0.018 mol of compound **1** and 1.39 g, 0.018 mol of pyridine) in 20 ml of CH_2Cl_2 (20 °C) with intense argon bubbling. The reaction mixture was kept for two months under argon and then treated with water. The organic layer was separated and the solvent was removed *in vacuo* (12 Torr, 100 °C). The viscous residue was washed with hexane and dissolved in aqueous acetone. The solid compound that formed gradually was filtered off and washed with diethyl ether. The yield of compound **6** was 77% (3.77 g), mp 132 °C. Found (%): C, 52.92; H, 5.33; Cl, 13.11; P, 11.47. Calc. for $C_{12}H_{14}ClO_3P$ (%): C, 52.84; H, 5.14; Cl, 13.02; P, 11.38. The IR-spectroscopic characteristics (cm^{-1}) coincide with published data.[3] The yield of compound **7** was 3% (0.15 g), mp 120 °C.

Treatment of compound **7** with calcium hydrate in aqueous acetone followed by prolonged crystallization gave calcium complex **8**, yield 95% (0.15 g), mp 126 °C (decomp.). Found (%): C, 50.41; H, 5.49; P, 11.33; Ca, 2.47. Calc. for $C_{72}H_{82}CaCl_6O_{18}P_6 \cdot 2H_2O$ (%): C, 50.56; H, 5.03; P, 10.88; Ca, 2.34.

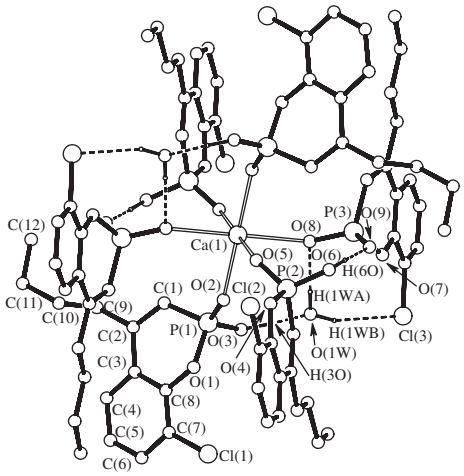


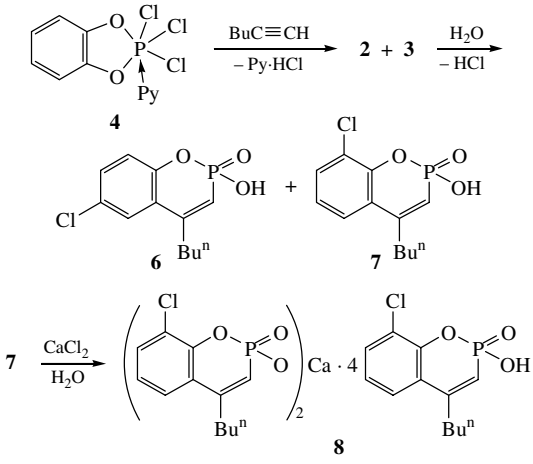
Figure 2 The general view of the crystal of complex **8** (hydrogen atoms are not shown). Selected bond lengths (Å): Ca(1)–O(2)#1 2.3309(18), Ca(1)–O(2) 2.3309(18), Ca(1)–O(5)#1 2.3491(17), Ca(1)–O(5) 2.3491(17), Ca(1)–O(8)#1 2.4289(19), Ca(1)–O(8) 2.4289(19), Cl(1)–C(7) 1.751(3), P(1)–O(2) 1.4824(19), P(1)–O(3) 1.554(2), P(1)–O(1) 1.6107(19), P(1)–C(1) 1.757(3), O(1)–C(8) 1.392(3); selected bond angles (°): O(2)#1–Ca(1)–O(5)#1 92.55(6), O(2)–Ca(1)–O(5)#1 87.45(6), O(2)#1–Ca(1)–O(5) 87.45(6), O(2)–Ca(1)–O(5) 92.55(6), O(5)#1–Ca(1)–O(5) 180.00(7), O(2)#1–Ca(1)–O(8)#1 91.73(7), O(2)–Ca(1)–O(8)#1 88.27(7), O(5)#1–Ca(1)–O(8)#1 85.84(6), O(5)–Ca(1)–O(8)#1 94.16(7), O(2)#1–Ca(1)–O(8) 88.27(7), O(2)–Ca(1)–O(8) 91.73(7), O(5)#1–Ca(1)–O(8) 94.16(7), O(5)–Ca(1)–O(8) 85.84(7), O(8)#1–Ca(1)–O(8) 180.0(1), O(2)–P(1)–O(3) 113.6(1), O(2)–P(1)–O(1) 108.4(1), O(3)–P(1)–O(1) 106.2(1), O(2)–P(1)–C(1) 117.0(1), O(3)–P(1)–C(1) 107.7(1), O(1)–P(1)–C(1) 102.9(1). The atoms with #1 are obtained from the basic ones by the symmetry operation ($-x + 1, -y + 1, -z + 1$).

containing six molecules of phosphorinine **7** as ligands. The cell also contains two solvation water molecules (Figure 2).

Note that the use of phosphorane–pyridine *ate*-complex **4** in the reaction with phenylacetylene is more preferred than the use of a twofold excess of the latter, since it becomes unnecessary to purify the reaction mixture from 2-chlorohex-1-ene, a reaction product of the original acetylene with HCl.

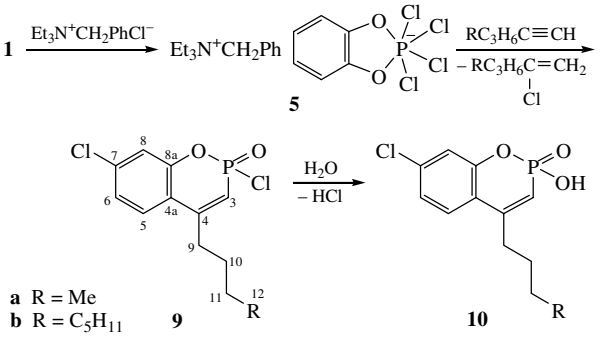
It was found that the reaction of anionic phosphorate **5** with alk-1-ynes gives predominantly benzophosphorinines **9** (Scheme 3), in which the chlorine atom is located at the *meta* position with respect to the endocyclic oxygen atom of the phosphorinine heterocycle.§ Chlorophosphorinine **2** is formed as a minor compound.

Compounds **9** manifest themselves in the ^{31}P NMR spectrum as doublets with δ_P 19.0–19.2 ($^2J_{PCH}$ 23.6–24.5 Hz). In order to study the structures of phosphorinines **9** by ^{1}H and ^{13}C NMR spectroscopy in more detail, they were hydrolysed to more stable phosphonic acids **10**,§ which showed doublets with δ_P 6.5–7.0



Scheme 2

($^2J_{PCH}$ 17.5–17.8 Hz) in the ^{31}P NMR spectra. Compounds **10** show signals of the trisubstituted phenylene moiety in the downfield region of ^{1}H NMR spectra; these signals are consistent with the presence of a chlorine atom in the ring. In order to determine its position, ^{13}C and ^{13}C-{^{1}H} NMR spectra were recorded. They contained a singlet at δ_C 134–135 corresponding to the C^7 atom. The downfield chemical shift of this signal and its shape in the ^{13}C NMR spectrum (doublet of doublets of doublets) suggest the *meta* orientation of chlorine with respect to the O^1 oxygen.



Scheme 3

Thus, the reaction with alk-1-ynes to give derivatives of benzo[*e*]-1,2-oxaphosphorinines can also be carried out using hexacoordinate phosphorus derivatives, *viz.*, *ate*-complexes based on 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole. A distinctive feature of the process using benzyltriethylammonium phenylenedioxytetrachlorophosphate is that chlorination of the benzo moiety occurs at the *meta* position with respect to the oxygen and carbon atoms of the resulting phosphorinine heterocycle. The use of the *ate*-complex of 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole with pyridine in the reaction with alkynes is preferable for the synthesis of 6-chloro substituted benzo[*e*]-1,2-oxaphosphorinines since it allows one to avoid using an excess of acetylene and formation of styrenes.

Online Supplementary Materials

Supplementary data associated with this article (NMR data for compounds **7** and **8**) can be found in the online version at doi:10.1016/j.mencom.2007.11.009.

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§ *Reaction of dioxaphosphole* **1** *with hex-1-yne in the presence of benzyltriethylammonium chloride.* A solution of hex-1-yne (5.04 ml, 0.043 mol) in 10 ml of CH_2Cl_2 was added to *ate*-complex **5** (5.4 g, 0.022 mol of compound **1** and 5.0 g, 0.022 mol of benzyltriethylammonium chloride) in 30 ml of CH_2Cl_2 (20 °C) with intense argon bubbling. The reaction mixture was kept for two months under argon and then treated with water. The organic layer was separated and the solvent was removed *in vacuo* (12 Torr, 100 °C). The viscous residue was washed with hexane and dissolved in aqueous acetone. The solid compound that formed gradually was filtered off and washed with diethyl ether. The yield of 4-butyl-7-chloro-2-hydroxy-2-oxobenzo[*e*]-1,2-oxaphosphorinine **10a** was 59% (3.54 g), mp 141–142 °C. Found (%): C, 52.77; H, 5.35; Cl, 13.27; P, 11.09. Calc. for $C_{12}H_{14}ClO_3P$ (%): C, 52.84; H, 5.14; Cl, 13.02; P, 11.38. IR (ν/cm^{-1}): 3069, 2670–2715 (very br.), 2330–2340 (very br.), 2150–2180 (very br.), 1651–1670, 1601, 1551, 1486, 1421, 1405, 1354, 1312, 1295, 1200–1210, 1143, 1085, 1040, 1007, 987, 961, 891, 863, 824, 773, 746, 714, 660, 627, 602, 531, 509, 482, 436.^{1}H NMR ([$^2H_6$]DMSO, 45 °C) δ: 8.65 (very br. s, OH), 7.72 (d, H^5, $^3J_{H^6CCH^5}$ 8.5 Hz), 7.40 (br. s, H^8), 7.33 (br. d, H^6, $^3J_{H^5CCH^6}$ 8.5 Hz), 6.25 (d, H^3, $^2J_{PCH^3}$ 17.6 Hz), 2.71 (br. t, C^{9}H$_2$, $^3J_{H^{10}CCH^9}$ 7.2 Hz), 1.51 (m, C^{10}H$_2$, $^3J_{H^9CCH^{10}}$ 7.2 Hz, $^3J_{H^{11}CCH^{10}}$ 7.2 Hz), 1.43 (m, C^{11}H$_2$, $^3J_{H^{11}CCH^{10}}$ 7.2 Hz, $^3J_{H^{12}CCH^{10}}$ 7.2 Hz), 0.98 (t, C^{12}H$_3$, $^3J_{H^{12}CCH^{10}}$ 7.2 Hz). ^{13}C NMR ([$^2H_6$]DMSO, 45 °C) δ: 113.95 [ddt (d), C^3, $^1J_{PC^3}$ 170.6 Hz, $^1J_{HC^3}$ 161.9 Hz, $^3J_{HC^9CC^3}$ 5.7 Hz], 151.58 [m (s), C^4], 121.07 [m (d), C^{4a}, $^3J_{PCCC^{4a}}$ 17.4 Hz], 128.29 [d (s), C^5, $^1J_{HC^5}$ 163.1 Hz], 123.92 [dd (s), C^6, $^1J_{HC^6}$ 169.2 Hz, $^3J_{HC^8CC^6}$ 5.3 Hz], 134.83 [ddd (s), C^7, $^3J_{HC^5CC^7}$ 13.4 Hz, $^2J_{HCC^7}$ 3.8–4.0 Hz, $^2J_{HCC^7}$ 4.6–4.8 Hz], 119.50 [ddd (d), C^8, $^1J_{HC^8}$ 168.3 Hz, $^3J_{POCC^8}$ 6.6 Hz, $^3J_{HC^6CC^8}$ 6.2–6.4 Hz], 152.26 [ddd (d), C^{8a}, $^2J_{HC^8C^{8a}}$ 5.0–6.0 Hz, $^3J_{HC^5CC^{8a}}$ 10.0–11.0 Hz, $^2J_{POC^{8a}}$ 7.2 Hz], 34.07 [tdm (d), C^9, $^1J_{HC^9}$ 127.0–128.0 Hz, $^3J_{PCCC^9}$ 17.4 Hz], 30.33 [ddm (s), C^{10}, $^1J_{HC^{10}}$ 122.2 Hz, $^1J_{HC^{10}}$ 126.3 Hz], 22.28 [ddm (s), C^{11}, $^1J_{HC^{11}}$ 122.1 Hz, $^1J_{HC^{11}}$ 125.3 Hz, $^2J_{HCC^{11}}$ 3.0–4.0 Hz, $^2J_{HCC^{11}}$ 3.0–4.0 Hz, $^3J_{HCCC^{11}}$ 3.0–4.0 Hz], 14.20 [qm (s), C^{12}, $^1J_{HC^{12}}$ 124.5 Hz, $^2J_{HCC^{12}}$ 4.0–4.1 Hz, $^3J_{HCCC^{12}}$ 4.0–4.1 Hz]. ^{31}P NMR ([$^2H_6$]DMSO, 45 °C) δ: 6.9 (d, 17.6 Hz). MS, *m/z* (the *m/z* values are given for ions containing the most widespread isotopes): 274, 272 [M]$^{+\cdot}$, 237 [M$^{+\cdot}$ – Cl], 230 [M$^{+\cdot}$ – C_3H_6], 212, 183, 165, 149.

The reaction of dioxaphosphole **1** with dec-1-yne in the presence of benzyltriethylammonium chloride was carried out similarly. The yield of 7-chloro-2-hydroxy-4-octyl-2-oxobenzo[*e*]-1,2-oxaphosphorinine **10b** was 53% (3.83 g), mp 104–106 °C. Found (%): C, 58.19; H, 6.77; P, 9.35. Calc. for $C_{16}H_{22}ClO_3P$ (%): C, 58.45; H, 6.70; P, 9.44. ^{1}H NMR ([$^2H_6$]DMSO, 45 °C) δ: 7.61 (d, H^5, $^3J_{H^6CCH^5}$ 8.8 Hz), 7.23 (d, H^8, $^4J_{H^6CCCH^8}$ 2.2 Hz), 7.20 (dd, H^6, $^3J_{H^5CCH^6}$ 8.8 Hz, $^4J_{H^8CCCH^6}$ 2.2 Hz), 6.13 (d, H^3, $^2J_{PCH^3}$ 17.5 Hz), 2.61 (br. t, C^{9}H$_2$, $^3J_{H^{10}CCH^9}$ 7.9 Hz), 1.51 (m, C^{10}H$_2$, $^3J_{H^9CCH^{10}}$ 7.9 Hz, $^3J_{H^{11}CCH^{10}}$ 7.5 Hz), 1.33 (C^{11}H$_2$, $^3J_{H^{12}CCH^{11}}$ 7.2 Hz, $^3J_{H^{10}CCH^{11}}$ 7.5 Hz), 1.23–1.25 (m, C^{12}H$_2$, C^{13}H$_2$, C^{14}H$_2$, C^{15}H$_2$), 0.82 (t, C^{16}H$_3$, $^3J_{H^{15}CCH^{16}}$ 7.0 Hz). ^{13}C NMR ([$^2H_6$]DMSO, 45 °C) δ: 113.47 [ddt (d), C^3, $^1J_{PC^3}$ 171.3 Hz, $^1J_{HC^3}$ 161.3 Hz, $^3J_{HC^9CC^3}$ 5.7 Hz], 151.25 [m (s), C^4], 120.80 [m (d), C^{4a}, $^3J_{PCCC^{4a}}$ 17.2 Hz, $^3J_{HC^3CC^{4a}}$ 9.0 Hz, $^3J_{HC^5CC^{4a}}$ 8.7–9.0 Hz, $^3J_{HC^8CC^{4a}}$ 8.7–9.0 Hz, $^3J_{HC^9CC^{4a}}$ 3.5–3.6 Hz], 127.79 [d (s), C^5, $^1J_{HC^5}$ 162.3 Hz], 123.44 [dd (s), C^6, $^1J_{HC^6}$ 169.4 Hz, $^3J_{HC^8CC^6}$ 5.2 Hz], 134.58 [ddd (s), C^7, $^3J_{HC^5CC^7}$ 13.2 Hz, $^2J_{HCC^7}$ 3.3 Hz, $^2J_{HCC^7}$ 4.1 Hz], 119.12 [dddd (d), C^8, $^1J_{HC^8}$ 168.4 Hz, $^3J_{POCC^8}$ 7.4 Hz, $^3J_{HC^6CC^8}$ 5.6 Hz, $^4J_{HC^5CCC^8}$ 1.0 Hz], 152.06 [ddd (d), C^{8a}, $^3J_{HC^5CC^{8a}}$ 9.0–10.0 Hz, $^2J_{POC^{8a}}$ 7.4 Hz, $^2J_{HC^8C^{8a}}$ 5.0–6.0 Hz], 34.15 [tdm (d), C^9, $^1J_{HC^9}$ 127.5 Hz, $^3J_{PCCC^9}$ 17.7 Hz, $^3J_{HCCC^9}$ 3.1–4.0 Hz, $^3J_{HCCC^9}$ 3.1–4.0 Hz, $^2J_{HCC^9}$ 3.1–4.0 Hz], 31.54 [br. tm (s), C^{10}, $^1J_{HC^{10}}$ 126.7 Hz], 29.06 (br. tm, C^{11}, $^1J_{HC^{11}}$ 125.0–127.0 Hz), 28.93 (br. tm, C^{12}, $^1J_{HC^{12}}$ 125.0–127.0 Hz), 28.92 (br. tm, C^{13}, $^1J_{HC^{13}}$ 125.0–127.0 Hz), 27.91 (br. tm, C^{14}, $^1J_{HC^{14}}$ 125.0–127.0 Hz), 22.32 [tm (s), C^{15}, $^1J_{HC^{15}}$ 124.8 Hz], 13.88 [br. qm (s), C^{12}, $^1J_{HC^{12}}$ 124.2 Hz]. ^{31}P NMR ([$^2H_6$]DMSO, 45 °C) δ: 6.9 (d, 17.5 Hz). IR (ν/cm^{-1}): 3109, 3046, 2725, 2671 (very br.), 2000–2200 (very br.), 1650–1670 (br.), 1601, 1549, 1487, 1416, 1346, 1293, 1196, 1188 (sh.), 1145, 1084, 1017, 962, 892, 863, 824, 804, 774, 753, 723, 663, 628, 601, 545, 523, 513, 465, 443, 425. MS, *m/z* (the m/z values are given for ions containing the most widespread isotopes): 330 (1.14), 328 (2.90) [M]$^{+\cdot}$ ($C_{16}H_{22}ClO_3P$), 299 (0.39) [M$^{+\cdot}$ – C_2H_5]$^+$, 293 (1.08) [M$^{+\cdot}$ – Cl]$^+$, 285 (0.59) [M$^{+\cdot}$ – C_3H_7]$^+$, 271 (0.84) [M$^{+\cdot}$ – C_4H_9]$^+$, 230 (100) [M$^{+\cdot}$ – C_7H_{14}]$^{+\cdot}$.