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Reactions in the chrysenequinone–phenylacetylene–phosphorus trichloride system: formation and crystal structure of 2,7-dichloro-2-oxo-4-phenylbenzo[*o*]-1,2-oxaphosphatriphenylene

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The reaction of chrysenequinone with phenylacetylene in the presence of phosphorus trichloride leads to the formation of a new phosphorus heterocycle, 2,7-dichloro-2-oxo-4-phenylbenzo[*o*]-1,2-oxaphosphatriphenylene, whose structure was established by NMR spectroscopy and single crystal X-ray diffraction.

The reactions of *P*,*P*,*P*-trichlorobenzo[*d*]-1,3,2-dioxaphosphole with arylacetylenes, unlike PCl_5, lead to the formation of benzo[*d*]-1,2-oxaphosphorinine derivatives,[1,2] which are phosphorus-containing analogues of coumarins, in high yields. A similar synthetic result can be obtained when the composition of *ortho*-quinone–phosphorus trichloride is used instead of a P^V derivative. For example, new phosphorus heterocycles, 4-aryl-1,2-oxaphosphatriphenylene derivatives,[3,4] were obtained in the reaction of phenanthrenequinone with arylacetylene in the presence of phosphorus trichloride.

Here we attempted to spread this approach to asymmetrical chrysenequinone **1**.[5] The staying of the mixture of phenylacetylene, quinone **1** and PCl_3 during a week in CH_2Cl_2 affords a crystalline compound,[†] which exhibits a singlet with δ_P 16.4 ppm ($^2J_{PCH}$ 28.0 Hz) in the ^{31}P NMR spectrum. There is a doublet with a similar coupling constant in the low-field region of the ^{1}H NMR spectrum (δ 6.73 ppm) of this species. Its mass spectrum contains the molecular ion peak of 461, corresponding to $C_{26}H_{15}Cl_2O_2P$; that is, a formation of three molecules addition product minus HCl one occurs. Taking into account the ^{1}H and ^{13}C NMR data and published results,[1–4] the structure of benzo[*o*]-1,2-oxaphosphatriphenylene **2** was assigned to the isolated compound. Its formation likely occurs *via* intermediate phosphorane **3**. The structure of **2** was fully confirmed by single crystal X-ray diffraction.[‡] The geometry of the molecule forming the solvate with $CDCl_3$ and its selected parameters (bond distances, bond and torsion angles) are shown in Figure 1. The molecule contains a chlorine atom at the 7-position of benzo[*o*]-1,2-oxaphosphatriphenylene. The heterocycle of **2** contains the O(1)C(12b)C(4a)C(4) and P(2)C(3)C(4)C(4a) planar fragments [that are planar within 0.046(4) and 0.033(4) Å], from which atoms C(3), P(2), O(1) and C(12b) are deviated on the one side and on various distances, namely, –0.418(4) Å [C(3)], –0.897(1) Å [P(2)], 0.811(3) Å [O(1)], 0.478(4) Å [C(12b)]; that is, it has a distorted (asymmetrical) boat conformation. The dihedral angle between these planar fragments is 19.8(4)°. The atoms O(2) and Cl(2) are deviated from the O(1)C(12b)C(4a)C(4) and P(2)C(3)C(4)C(4a) planes by –0.713(3), –2.774(1) Å and 0.625(3), –1.833(1) Å, respectively, that is, the O(2) atom occupies an equatorial position and the Cl(2) atom is in an apical one.

[†] *2,7-Dichloro-2-oxo-4-phenylbenzo[*o*]-1,2-oxaphosphatriphenylene* **2**. The mixture of 1.5 g of 5,6-chrysenequinone,[5] 1.89 ml of phenylacetylene and 40 ml of CH_2Cl_2 was added dropwise to 1.02 ml of PCl_3 (20 °C). The reaction mixture was allowed to stand for 4 days; then, it was filtered in an argon atmosphere and 1.7 g (63%) of **2** was obtained as small hygroscopic crystals with mp 290–293 °C (in a capillary). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 9.70 [br. d, H(16), $^3J_{H(15)CCH(16)}$ 8.0 Hz], 8.71 [br. s, H(8)], 8.62 [br. d, H(9), $^3J_{H(10)CCH(9)}$ 8.8 Hz], 8.19 [br. d, H(10), $^3J_{H(9)CCH(10)}$ 8.8 Hz], 8.06 [br. d, H(13), $^3J_{H(14)CCH(13)}$ 7.6 Hz], 7.07, 7.20–7.32, 7.42–7.47 [3m, Ph, H(5), H(6)], 7.74–7.75 [m, H(14), $^3J_{H(13)CCH(14)}$ 7.6 Hz, $^3J_{H(15)CCH(14)}$ 7.3 Hz], 7.83–7.84 [m, H(15), $^3J_{H(16)CCH(15)}$ 8.0 Hz, $^3J_{H(14)CCH(15)}$ 7.3 Hz], 6.73 [d, H(3), $^2J_{PCH}$ 28.0 Hz]. ^{31}P NMR (162.0 MHz, $CDCl_3$) δ_P: 16.4 (d, $^2J_{PCH}$ 28.0 Hz).

The melting points were measured using a Boetius melting point apparatus. NMR spectra were recorded on Bruker WM-250 (250 MHz, ^{1}H), MSL-400 (100.6 MHz, ^{13}C; 162.0 MHz, ^{31}P), CXP-100 (36.48 MHz) and Avance-600 (600 MHz, ^{1}H; 150.9 MHz, ^{13}C) spectrometers. 2D-experiments were conducted on a Bruker Avance-600 spectrometer. 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 deuterated solvent signal. The IR spectrum was recorded on a Bruker Vector instrument in Nujol.

[‡] The X-ray analysis of compound **2** was carried out on an automatic Enraf-Nonius CAD-4 diffractometer at –150 °C. Crystals of compound **2** $C_{26}H_{14}Cl_2O_2P\cdot CDCl_3$, triclinic, $a = 7.777(4)$ Å, $b = 11.067(2)$ Å and $c = 14.947(4)$ Å, $\alpha = 72.10(2)°$, $\beta = 80.39(4)°$, $\gamma = 81.93(3)°$, V = = 1201.6(8) Å^3, $Z = 2$, $M = 579.66$, $d_{calc} = 1.602$ g cm^{-3}, $F(000) = 586$, space group $P\bar{1}$. Cell parameters and intensities of 4830 independent reflections, from which 2959 with $I \geq 3\sigma$, were measured on an Enraf–Nonius CAD-4 diffractometer in the $\omega/2\theta$-scan mode, $2\theta \leq 26.3°$ (MoKα radiation, graphite monochromator). The intensity falling was not observed at three control measurements, the account of absorption was not carried out because of its smallness (μ_{Mo} 6.97 cm^{-1}). The structure was solved by a direct method using the SIR program[7] and refined in isotropic and anisotropic approximations. Subsequently, the hydrogen atoms were solved from difference Fourier maps, and the contribution of structural factors was calculated isotropically in the last cycles. The final residuals were $R = 0.030$, $R_w = 0.054$ and $R = 0.061$ on 2951 independent reflections $F^2 \geq 3\sigma^2$. All calculations were performed on an Alpha Station 200 computer using the MolEN program package.[8]

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 270214. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

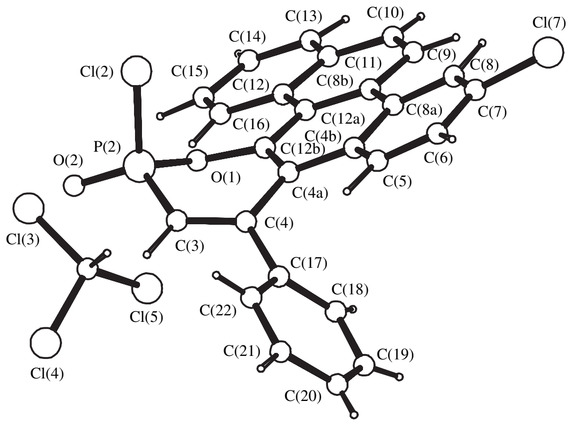
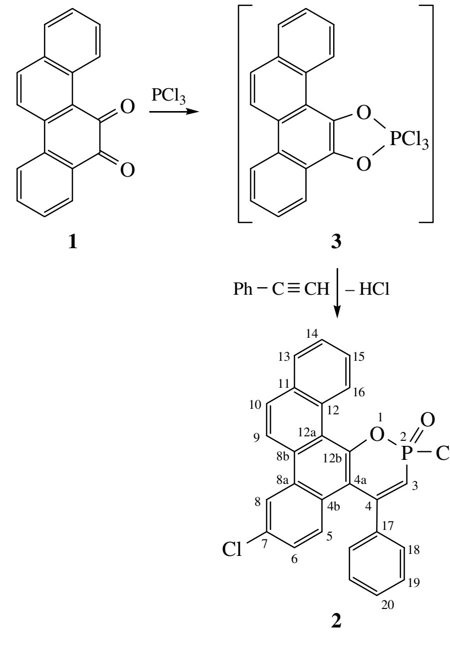
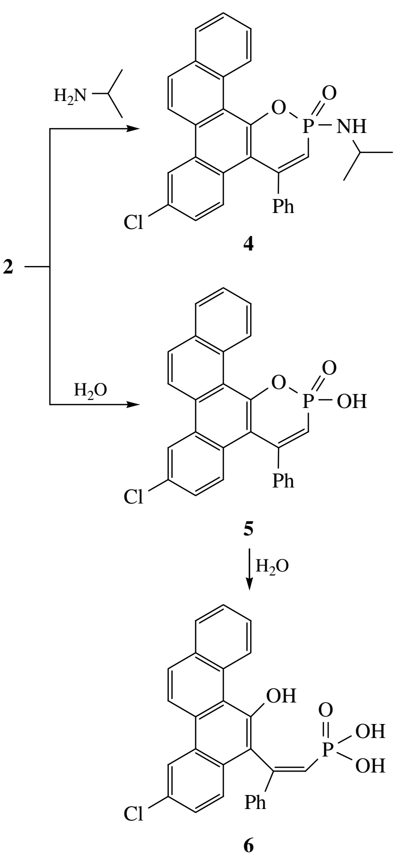


Figure 1 Molecular structure of the solvate of compound **2** with $CDCl_3$. Selected bond lengths (Å): Cl(2)–P(2) 2.010(2), Cl(7)–C(7) 1.719(4), P(2)–O(1) 1.586(3), P(2)–O(2) 1.471(3), P(2)–C(3) 1.740(5), O(1)–C(12b) 1.398(4), C(3)–C(4) 1.353(5), C(4b)–C(4a) 1.451(5), C(4a)–C(12b) 1.370(6); selected bond angles (°): Cl(2)–P(2)–O(1) 103.2(1), Cl(2)–P(2)–O(2) 112.1(2), Cl(2)–P(2)–C(3) 108.5(2), O(1)–P(2)–O(2) 110.6(2), O(1)–P(2)–C(3) 101.9(2), O(2)–P(2)–C(3) 119.0(2), P(2)–O(1)–C(12b) 120.9(3), P(2)–C(3)–C(4) 117.6(3), C(4a)–C(4b)–C(5) 122.3(4), C(3)–C(4)–C(4a) 121.6(4), O(1)–C(12b)–C(4a) 118.7(4), O(1)–C(12b)–C(12a) 116.6(3), C(4a)–C(12b)–C(12a) 124.8(3); selected torsion angles (°): Cl(2)–P(2)–O(1)–C(12b) –65.0(3), O(2)–P(2)–O(1)–C(12b) 174.9(3), C(3)–P(2)–O(1)–C(12b) 47.5(3), Cl(2)–P(2)–C(3)–C(4) 81.6(4), O(1)–P(2)–C(3)–C(4) –26.8(4), O(2)–P(2)–C(3)–C(4) –148.7(3), P(2)–O(1)–C(12b)–C(4a) –31.9(5), P(2)–O(1)–C(12b)–C(12a) 149(3), P(2)–C(3)–C(4)–C(4a) –6.9(6), C(5)–C(4b)–C(4a)–C(12b) –169.1(4), C(3)–C(4)–C(4a)–C(12b) 30.0(6), C(17)–C(4)–C(4a)–C(12b) –145.2(4), C(3)–C(4)–C(17)–C(18) –135.6(4), C(3)–C(4)–C(17)–C(22) 40.0(6).

The phenyl group at the 4-position is turned along the P(2)C(3)–C(4)C(4a) plane on an angle of 40.0(6)° [C(3)C(4)C(17)C(22)]. The chrysene system is twisted to some extent, and a dihedral angle between the C(4b)C(5)C(6)C(7)C(8)C(8a) benzo fragment [which is planar within 0.011(5) Å] and the C(8b)C(9)C(10)–C(11)C(13)C(14)C(15)C(16)C(12) naphtho fragment [which is planar within 0.024(5) Å] is equal to 7.3(2)°.

Amide **4**[§] was obtained by the isopropylamine treatment of compound **2**. Its cyclic nature was established using ^{1}H NMR spectra [the $^2J_{POC(12b)}$ and $^3J_{PCCC(4a)}$ 16.6 Hz coupling constants, indicating two PC(3)C(4)C(4a) and POC(12b)C(4a) pathways for the spin–spin interaction]. The full interpretation of the ^{13}C-{^{1}H} spectrum of amide **4** was made taking into account both the signals multiplicity caused by the carbon–proton and carbon–phosphorus coupling constants in ^{13}C NMR spectrum and published data.[1–4]





[§] *7-Chloro-2-isopropylamino-2-oxo-4-phenylbenzo[*o*]-1,2-oxaphosphatriphenylene* **4**. The mixture of 0.65 ml of isopropylamine and 10 ml of benzene was added to **2** (1.5 g in 30 ml of dry benzene) and allowed to stand for 2 days. The precipitate obtained after 2 days was filtered off, washed with alkaline water (pH 8) and dried in air. Amide **4** was obtained as white powder (1.26 g, 80%) with mp 299 °C. ^{1}H NMR (400 MHz, [$^2H_6$]DMSO, 40 °C) δ: 9.86 [ddd, H(16), $^3J_{H(15)CCH(16)}$ 6.2–6.3 Hz, $^4J_{H(14)CCCH(16)}$ 3.3 Hz, $^5J_{H(13)CCCCH(16)}$ 0.7 Hz], 8.93 [br. dd, H(8), $^4J_{H(6)CCCH(8)}$ 1.5 Hz, $^5J_{H(8)CCCCH(9)}$ 1.1 Hz], 8.92 [br. dd, H(9), $^3J_{H(10)CCH(9)}$ 9.0 Hz], 8.27 [br. d, H(10), $^3J_{H(9)CCH(10)}$ 9.0 Hz], 8.19 [br. dd, H(13), $^3J_{H(14)CCH(13)}$ 6.0 Hz], 7.76–7.77 [m, H(14), H(15)], 7.31 [d, H(5), B-part of AB-spectrum, $^3J_{H(6)CCH(5)}$ 8.8 Hz], 7.27 [br. dd, H(6), A-part of AB-spectrum, $^3J_{H(5)CCH(6)}$ 8.8 Hz, $^4J_{H(8)CCCH(6)}$ 1.5 Hz], 7.27 and 7.40 (br. m, Ph), 6.64 [d, H(3), $^2J_{PCH}$ 22.0 Hz], 5.68 (br. m, PNH), 3.58 (br. m, NCH), 1.21 and 1.22 (2d, Me, $^3J_{HCCH}$ 6.5 Hz). ^{13}C NMR (the view of signal in ^{13}C-{^{1}H} NMR spectrum is given in parentheses) (100.6 MHz, [$^2H_6$]DMSO, 70 °C) δ: 119.28 [dd (d), C(3), $^1J_{PC}$ 163.0 Hz, $^1J_{HC}$ 163.5 Hz], 152.24 [m (br. s), C(4)], 115.49 [m (d), C(4a), $^3J_{PCCC}$ 16.6 Hz], 128.48 and 128.78 [2m (2s) C(4b), C(12)], 128.88 [d (s), C(5), $^1J_{HC}$ 163.9 Hz], 125.54 [dd (s), C(6), $^1J_{HC}$ 168.2 Hz, $^3J_{HC(8)CC(6)}$ 5.8 Hz], 130.09 [ddd (s), C(7), $^3J_{HC(5)CC(7)}$ 11.0 Hz, $^2J_{HCC}$ 6.0 Hz, $^2J_{HCC}$ 4.1 Hz], 122.93 [dd (s), C(8), $^1J_{HC}$ 164.9 Hz, $^3J_{HC(6)CC(8)}$ 3.8 Hz], 127.05 [br. dd (s), C(8a), $^3J_{HC(5)CC(8a)}$ 7.7 Hz, $^3J_{HC(9)CC(8a)}$ 6.3 Hz], 130.54 [m (s), C(8b), $^3J_{HC(10)CC(8b)}$ 9.0 Hz, $^3J_{HC(8)CC(8b)}$ 3.0 Hz, $^2J_{HC(9)C(8b)}$ 1.4 Hz], 120.91 [d (s), C(9), $^1J_{HC}$ 157.5 Hz], 128.49 [is superimposed on C(19), (s), C(10)], 132.95 [m (s), C(11)], 120.68 [m (d), C(12a), $^3J_{POCC}$ 4.9 Hz], 149.36 [d (d), C(12b), $^2J_{POC}$ 9.9 Hz], 127.59 [br. dm (s), C(13), $^1J_{HC}$ 164.0 Hz, $^3J_{HCCC}$ 3.7–4.0 Hz, $^3J_{HCCC}$ 3.2–3.5 Hz], 126.66 and 126.69 [2dd (2s), C(14), C(15), $^1J_{HC}$ 160.0 Hz and $^3J_{HCCC}$ 7.3 Hz, $^1J_{HC}$ 159.0 Hz and $^3J_{HCCC}$ 7.4 Hz], 130.29 [dd (s), C(16), $^1J_{HC}$ 162.0 Hz, $^3J_{HC(14)CC(16)}$ 5.7 Hz], 141.63 [m (d), C(17), $^3J_{PCCC}$ 18.2 Hz], 126.96 [br. dm (s), C(18), $^1J_{HC}$ 159.3–160.2 Hz, $^3J_{HCCC}$ 6.5–7.0 Hz, $^3J_{HCCC}$ 6.5–7.0 Hz], 128.49 [br. dd (s), C(19), $^1J_{HC}$ 159.0–160.0 Hz, $^3J_{HCCC}$ 7.3 Hz], 128.32 [dt (s), C(20), $^1J_{HC}$ 161.0 Hz, $^3J_{HCCC}$ 7.9 Hz], 42.65 [dm (s), NCH, $^1J_{HC}$ 137.6 Hz, $^2J_{PNC}$ 0 Hz, $^2J_{HNC}$ 4.9 Hz, $^2J_{HCC}$ 3.7 Hz], 24.80 and 24.51 [2br. qm (2d), Me, $^1J_{HC}$ 125.0 Hz and $^3J_{PNCC}$ 4.0 Hz, $^1J_{HC}$ 122.4 Hz and $^3J_{PNCC}$ 6.1 Hz]. ^{31}P NMR (162.0 MHz, [$^2H_6$]DMSO) δ_P: 12.5. IR (ν/cm^{-1}): 3158 (NH), 1618, 1589, 1565, 1542, 1515, 1399, 1303, 1244, 1231, 1200, 1180, 1161, 1133, 1106, 1078, 1048, 994, 954, 906, 864, 847, 825, 792, 762, 745, 714, 701, 681, 652, 619, 582, 572, 549, 521, 505, 477, 430. Found (%): C, 72.18; H, 4.77; P, 6.51. Calc. for $C_{29}H_{22}ClNO_2P$ (%): C, 72.12; H, 4.56; P, 6.42.

The hydrolysis of chloride **2** under mild conditions (under air in ether solution) also affords cyclic derivative **5**,[¶] the structure of which was confirmed by ^{31}P and ^{1}H NMR spectroscopy. The $^{2}J_{\mathrm{PCH}}$ coupling constant of 21.3 Hz indicates the retention of the phosphorine heterocycle.[1–4] However, the cycle is gradually opening under the long keeping up in moist DMSO, and the formation of substituted vinylphosphonic acid **6** occurs. The $^{2}J_{\mathrm{PCH}}$ coupling constant decreased up to 15.7 Hz. The structure of compound **6**[††] was correctly determined by the 1D and 2D ^{1}H, ^{13}C-{^{1}H} NMR using COSY, NOESY ^{1}H-^{1}H and HETCOR ^{1}H–^{13}C (TOCSY, HMBC and HSQC) techniques.

Thus, the reaction in the chrysenequinone–phenylacetylene–phosphorus trichloride system leads to the formation of a new phosphorus heterocycle, 2,7-dichloro-2-oxo-4-phenylbenzo[*o*]-1,2-oxaphosphatriphenylene. The chlorination of the 7-position of the heterocycle proceeds. The reaction is promising for the functionalization of complex natural 1,2-quinones to structures with annelated 1,2-phosphorinine heterocycle. Recently, some of heterocycles annelated with chrysene were proposed as promising photochromic compounds.[6]

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References

1 V. F. Mironov, A. I. Konovalov, I. A. Litvinov, A. T. Gubaidullin, R. R. Petrov, A. A. Shtyrlina, T. A. Zyablikova, R. Z. Musin, N. M. Azancheev and A. V. Il’yasov, *Zh. Obshch. Khim.*, 1998, **68**, 1482 (*Russ. J. Gen. Chem.*, 1998, **68**, 1414).

2 V. F. Mironov, I. A. Litvinov, A. A. Shtyrlina, A. T. Gubaidullin, R. R. Petrov, A. I. Konovalov, N. M. Azancheev and R. Z. Musin, *Zh. Obshch. Khim.*, 2000, **70**, 1117 (*Russ. J. Gen. Chem.*, 2000, **70**, 1046).

3 V. F. Mironov, A. T. Gubaidullin, T. A. Baronova, F. F. Alekseev, I. A. Litvinov and A. I. Konovalov, *Zh. Obshch. Khim.*, 2000, **70**, 521 (*Russ. J. Gen. Chem.*, 2000, **70**, 486).

4 V. F. Mironov, F. F. Alekseev, A. A. Shtyrlina, N. M. Azancheev and A. I. Konovalov, *Zh. Obshch. Khim.*, 2000, **70**, 695 (*Russ. J. Gen. Chem.*, 2000, **70**, 646).

5 C. Graebe and F. Hönigsberger, *Liebigs Ann. Chem.*, 1900, **311**, 257.

6 T. Yamaguchi, Y. Fujita, H. Nakazumi, S. Kobatake and M. Irie, *Tetrahedron*, 2004, **60**, 9863.

7 A. Altomare, G. Cascarano, C. Giacovazzo and D. Viterbo, *Acta Crystallogr., Sect. A*, 1991, **47**, 744.

8 L. H. Straver and A. J. Schierbeek, *MolEN. Structure Determination System*, Nonius B.V., 1994.

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[¶] *7-Chloro-2-hydroxy-2-oxo-4-phenylbenzo[*o*]-1,2-oxaphosphatriphenylene* **5**. Chloride **2** (0.2 g) was dissolved in 10 ml of moist diethyl ether and allowed to stand for 8 h. Solvent was removed *in vacuo*, and compound **5** was obtained as white powder (0.17 g, 90%) with mp 329 °C. ^{1}H NMR (600 MHz, [^{2}H$_{6}$]DMSO, 50 °C) δ: 9.77 [br. d, H(16), $^{3}J_{\mathrm{H(15)CCH(16)}}$ 9.1 Hz], 8.98 [br. s, H(8)], 8.96 [d, H(9), $^{3}J_{\mathrm{H(10)CCH(9)}}$ 9.1 Hz], 8.28 [br. d, H(10), $^{3}J_{\mathrm{H(9)CCH(10)}}$ 9.1 Hz], 8.19 [br. d, H(13), $^{3}J_{\mathrm{H(14)CCH(13)}}$ 7.0 Hz], 7.82 [m, H(14), $^{3}J_{\mathrm{H(13)CCH(14)}}$ 7.0 Hz, $^{3}J_{\mathrm{H(15)CCH(14)}}$ 7.4 Hz], 7.78 [m, H(15), $^{3}J_{\mathrm{H(16)CCH(15)}}$ 9.1 Hz, $^{3}J_{\mathrm{H(14)CCH(15)}}$ 7.4 Hz], 7.24–7.27 [m, H^{p}, H^{m}, H(6)], 7.36–7.37 [m, H^{o}, H(5)], 6.77 [d, H(3), $^{2}J_{\mathrm{PCH}}$ 21.3 Hz]. ^{31}P NMR (36.48 MHz, [^{2}H$_{6}$]DMSO) δ_{P}: 4.8 (d, $^{2}J_{\mathrm{PCH}}$ 21.3 Hz). Found (%): C, 70.67; H, 3.79; P, 7.12. Calc. for $C_{26}H_{16}ClO_{3}P$ (%): C, 70.51; H, 3.62; P, 7.01.

[††] *2-(7-Chloro-11-hydroxychrysen-12-yl)-2-phenylvinylphosphonic acid* **6**. Compound **5** (0.17 g) was allowed to stand in moist DMSO for 4 days, and white powder of acid **6** (0.17 g, mp 247 °C) was obtained. ^{1}H NMR (600 MHz, [^{2}H$_{6}$]DMSO, 50 °C) δ: 10.00 [dd, H(16), $^{3}J_{\mathrm{H(15)CCH(16)}}$ 9.7 Hz, $^{4}J_{\mathrm{H(14)CCCH(16)}}$ 4.2 Hz], 8.84 [d, H(8), $^{4}J_{\mathrm{H(6)CCCH(8)}}$ 1.8 Hz], 8.83 [d, H(9), $^{3}J_{\mathrm{H(10)CCH(9)}}$ 9.2 Hz], 8.13 [d, H(10), $^{3}J_{\mathrm{H(9)CCH(10)}}$ 9.2 Hz], 8.07 [dd, H(13), $^{3}J_{\mathrm{H(14)CCH(13)}}$ 9.3 Hz, $^{4}J_{\mathrm{H(15)CCCH(13)}}$ 3.7 Hz], 7.65–7.67 [m, H(14), H(15)], 7.51 [d, H(5), $^{3}J_{\mathrm{H(6)CCH(5)}}$ 8.8 Hz], 7.43 [dd, H(6), $^{3}J_{\mathrm{H(5)CCH(6)}}$ 8.8 Hz, $^{4}J_{\mathrm{H(8)CCCH(6)}}$ 1.8 Hz], 7.25 (m, Ph), 6.95 [d, H(3), $^{2}J_{\mathrm{PCH}}$ 15.4 Hz]. ^{13}C-{^{1}H} NMR (150.9 MHz, [^{2}H$_{6}$]DMSO, 50 °C, interpretation was made taking into account COSY ^{1}H-{^{1}H} and COSY GP ^{1}H-{^{1}H} NMR experiments) δ: 124.69 [d, C(3), $^{1}J_{\mathrm{PC}}$ 183.5 Hz], 150.13 [d, C(4), $^{2}J_{\mathrm{PCC}}$ 5.0 Hz], 121.39 [d, C(4a), $^{3}J_{\mathrm{PCCC}}$ 7.4 Hz], 130.11 [s, C(4b)], 127.73 [s, C(5)], 127.43 [s, C(6)], 129.61 [s, C(7)], 123.07 [s, C(8)], 127.51 [s, C(8a)], 129.95 [s, C(8b)], 121.71 [s, C(9)], 129.39 [s, C(10)], 133.35 [s, C(11)], 130.83 [s, C(12)], 150.92 [d, C(12b), $^{4}J_{\mathrm{PCCCC}}$ 1.5 Hz], 128.74 [s, C(13)], 126.93 [s, C(14)], 127.09 [s, C(15)], 129.63 [s, C(16)], 139.99 [d, C(17), $^{3}J_{\mathrm{PCCC}}$ 20.8 Hz], 126.86 [s, C(18)], 129.15 [s, C(19)], 129.52 [s, C(20)]. ^{31}P NMR (36.48 MHz, [^{2}H$_{6}$]DMSO) δ_{P}: 13.0 (d, $^{2}J_{\mathrm{PCH}}$ 15.7 Hz). Found (%): C, 67.87; H, 4.12; P, 6.88. Calc. for $C_{26}H_{18}ClO_{4}P$ (%): C, 67.75; H, 3.91; P, 6.73.