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Synthesis of bis-phosphonium salts from 6-bromo-1,2-naphthoquinone and α,ω-bis(diphenylphosphino)alkanes

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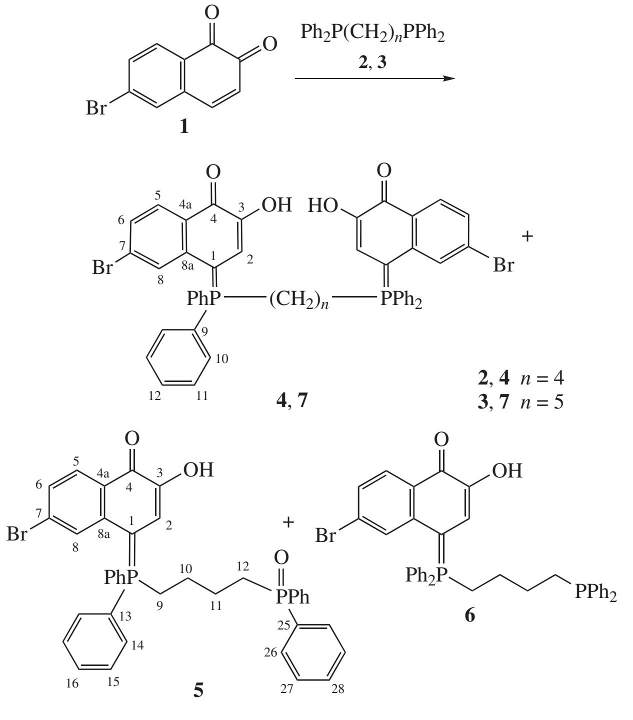
1,4-Bis(diphenylphosphino)butane and 1,5-bis(diphenylphosphino)pentane add two molecules of 6-bromo-1,2-naphthoquinone to afford bis-ylides which on treatment with protic acids are converted into the corresponding *P*,*P'*-bis(7-bromo-3,4-dihydroxy-1-naphthyl)-substituted bis-phosphonium salts.

Development of the efficient synthesis of multifunctional organophosphorus compounds is one of the important trends of organoelement chemistry. Phosphonium salts are of special interest since they can serve as diagnostic agents for tumor and antioxidants for cell mitochondria,[1–6] extragents,[7] organocatalysts,[8,9] phase transfer catalysts,[10] reagents for synthesis,[11–14] organogel gelators of silicates polymerization,[15] ionic liquids,[16–18] receptors of the selective anion recognition,[19] and additives for electrolytes in lithium batteries.[20] In this respect phosphonium derivatives bearing 1,2-dihydroxyarene or *ortho*-quinone fragments as substituents at phosphorus can be versatile precursors for the diverse heterocyclic compounds as well as promising ligands for metal complexes.[21–24]

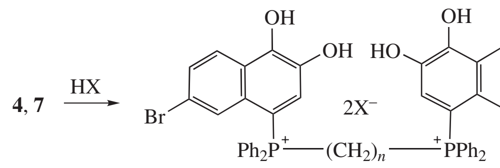
Recently, we have shown that 1,2-bis(diphenylphosphino)ethane having two tertiary phosphine fragments easily reacts with 6-bromo-1,2-naphthoquinone **1** to form a *P*-(7-bromo-3,4-dihyroxynaphth-1-yl)-substituted phosphonium salt with the participation of only one phosphorus atom of this bis-phosphine.[25] Meanwhile, the access to bridging *P*,*P'*-bis(7-bromo-3,4-dihydroxynaphth-1-yl)-substituted bis-phosphonium salt looks more challenging for the known useful properties of relative bis-catecholates.[26] We supposed that participation of only one phosphorus atom of 1,2-bis(diphenylphosphino)ethane in the reaction with quinone **1** is connected with steric hindrances caused by the short length of ethane-1,2-diyl spacer. In this work we used α,ω-bis(diphenylphosphino)alkanes **2** and **3** having longer spacers between phosphine moieties (Scheme 1). Indeed, reaction of quinone **1** with 1,4-bis(diphenylphosphino)butane **2** led to the expected bis-ylide **4** (53% yield). Two other compounds **5** (21% yield) and **6** (16% yield), whose formation during the process can be readily rationalized, were also isolated by the fractional crystallization.[†]



Scheme 1

[†] *(Butane-1,4-diyl)bis[(7-bromo-3-hydroxy-4-oxonaphthalen-1(4*H*)-ylidene)(diphenyl)phosphorane]* **4**. To a solution of quinone **1** (0.5 g, 2.10 mmol) in 20 ml of refluxing benzene, 1,4-bis(diphosphino)butane **2** (0.45 g, 1.05 mmol) was added in five portions during 30 min with intense bubbling of dry argon. The reaction occurred immediately. The reaction mixture turned black, and green solid of the product **4** was filtered off, recrystallized from chloroform and dried at 12 Torr, yield 0.50 g (53%), mp 180–183 °C. IR (ν/cm^{-1}): 3419 (OH), 1763, 1655, 1579, 1540, 1306, 1271, 1212, 1109, 1074, 1026, 994, 966, 895, 820, 742, 721, 692, 512. ^{1}H NMR (DMF-d_7) δ: 8.53 (d, H^6, $^3J_{\mathrm{HCCH}}$ 8.6 Hz), 8.37 (d, H^5, $^3J_{\mathrm{HCCH}}$ 8.9 Hz), 8.20 (br. s, H^8, overlaps with the signal of H^{12}), 8.20 (dt, H^{12}, $^3J_{\mathrm{HCCH}}$ 6.9 Hz, overlaps with the signal of H^8), 8.03 (m, H^{10}, H^{11}), 7.50 (d, H^2, $^3J_{\mathrm{PCCH}}$ 16.2 Hz), 2.74 (m, H^{13}), 2.15 (m, H^{14}). ^{13}C NMR (DMSO-d_6) δ_{C}: 164.30 [s (s), C^4], 143.89 [dd (d), C^3, $^3J_{\mathrm{PCCC}}$ 9.5 Hz, $^2J_{\mathrm{HCC}}$ 4.0 Hz], 134.32 [dt (br. s), C^{12}, $^1J_{\mathrm{HC}}$ 161.8 Hz, $^2J_{\mathrm{HCC}}$ 3.3 Hz], 133.39 [ddd (d), C^{10}, $^1J_{\mathrm{HC}}$ 165.1 Hz, $^2J_{\mathrm{PCC}}$ 9.5 Hz, $^3J_{\mathrm{HCCC}}$ 7.7 Hz], 131.77 [m (d), C^{8a}, $^2J_{\mathrm{PCC}}$ 7.7 Hz, overlaps with the signal of C^2], 130.83 [dd (d), C^2, $^1J_{\mathrm{HC}}$ 163.2 Hz, $^2J_{\mathrm{PC}}$ 9.2 Hz], 130.31 [ddd (d), C^{11}, $^3J_{\mathrm{PCCC}}$ 11.7 Hz, $^3J_{\mathrm{HCCC}}$ 8.1 Hz, $^3J_{\mathrm{HCCC}}$ 7.7 Hz], 129.48 [m (s), C^6, overlaps with the C^{11} signal], 128.90 [m (d), C^8, $^3J_{\mathrm{PCCC}}$ 4.0 Hz, overlaps with the components of C^{4a} and C^{11} signals], 127.88 [m (d), C^{4a}, $^3J_{\mathrm{PCCC}}$ 11.4 Hz], 127.59 [d (s), C^5, $^1J_{\mathrm{HC}}$ 167.6 Hz], 124.63 [m (d), C^9, $^1J_{\mathrm{PC}}$ 75.9 Hz], 122.36 [dd (br. d), C^1, $^1J_{\mathrm{PC}}$ 81.2 Hz, $^3J_{\mathrm{HCCC}}$ 4.0 Hz], 122.36 [dd (s), C^7, $^3J_{\mathrm{HCCC}}$ 5.8 Hz, $^2J_{\mathrm{HCC}}$ 2.2 Hz], 22.30–23.58 [br. dt (br. m), C^{13}, C^{14}]. ^{31}P / ^{31}P-{^{1}H} NMR (DMSO-d_6) δ_{P}: 19.4 [m (s)]. MS, *m/z*: 900.9 ($C_{48}H_{38}Br_2O_4P_2$). Found (%): C, 63.95; H, 4.15; Br, 17.74; P, 6.90. Calc. for $C_{48}H_{38}Br_2O_4P_2$ (%): C, 64.00; H, 4.22; Br, 17.77; P, 6.88.

P-*{4-[(7-Bromo-3-hydroxy-4-oxonaphthalen-1(4*H*)-ylidene)(diphenyl)-phosphoranyl]butyl}*-P,P-*diphenylphosphine oxide* **5** precipitated from the above filtrate after 24 h of standing. The crystals were filtered off and dried under reduced pressure (14 Torr). Yield 0.21 g (21%, excluding the solvated benzene molecules), mp 188–192 °C. IR (Nujol, ν/cm^{-1}): 3441 (OH), 1704, 1678, 1593, 1561, 1536, 1338, 1182, 1269 (P=O), 1119, 983, 964, 845, 747, 694, 555, 510. ^{1}H NMR (CDCl$_3$) δ: 8.47 (dd, H^6, $^3J_{\mathrm{HCCH}}$ 8.9 Hz, $^4J_{\mathrm{HCCCH}}$ 1.7 Hz), 7.70 (dt, H^{16}, $^3J_{\mathrm{HCCH}}$ 8.6 Hz, $^4J_{\mathrm{HCCCH}}$ 1.4 Hz,



8 $n = 4$, X = Br
9 $n = 4$, X = CF_3SO_3
10 $n = 5$, X = CF_3SO_3

Scheme 2

overlaps with H^{15} signal), 7.67 (dd, H^{15}, $^3J_{HCCH}$ 9.9 Hz, overlaps with H^{16} signal), 7.58 (ddd, H^{14}, $^3J_{PCCH}$ 12.9 Hz, $^3J_{HCCH}$ 4.8 Hz, $^4J_{HCCCH}$ 1.4 Hz), 7.51 (dt, H^{28}, $^3J_{HCCH}$ 7.2 Hz, $^4J_{HCCCH}$ 1.4 Hz), 7.45 (m, H^{26}, overlaps with H^{27} signal), 7.23 (dd, H^5, $^3J_{HCCH}$ 8.9 Hz, $^5J_{PCCCCH}$ 2.0 Hz), 7.12 (br. s, H^8), 6.94 (d, H^2, $^3J_{PCCH}$ 15.0 Hz), 2.93 (m, H^9), 1.77 (m, H^{10}, H^{11}), 2.20 (m, H^{12}). ^{31}P / ^{31}P-{^1H} NMR (DMSO-d_6) δ_P: 31.8 [m (s), 1P, P=O], 20.6 [m (s), 1P, P^+). MS, *m*/*z*: 677.0 $[M]^{+\bullet}$ ($C_{38}H_{33}BrO_3P_2$). Found (%): C, 73.49; H, 5.48; Br, 8.30; P, 6.70. Calc. for $C_{56}H_{51}BrO_3P_2$ (%): C, 73.60; H, 5.58; Br, 8.76; P, 6.79.

P-*(7-Bromo-3-hydroxy-4-oxonaphthalen-1(4*H*)-ylidene)*-P-*(4-diphenylphosphinobut-1-yl)*-P,P-*(diphenyl)phosphorane* **6** was obtained after slow evaporation of the solvent from the abovementioned filtrate (after isolation of compound **5**) as colourless crystals, yield 0.11 g (16%), mp 186–190 °C. IR (ν/cm^{-1}): 3612, 3545 (OH), 1573, 1538, 1460 (P–Ph), 1377, 1165, 1108, 1072, 994, 965, 819, 740, 721, 690, 516, 438. ^{31}P / ^{31}P-{^1H} NMR (DMSO-d_6) δ_P: 18.6 [m (s), 1P, P^{IV}], –15.6 [m (s), 1P, P^{III}].

(*Pentane-1,5-diyl)bis[(7-bromo-3-hydroxy-4-oxonaphthalen-1(4*H*)-ylidene)(diphenyl)phosphorane]* **7**. Yield 81%, mp 185–188 °C. For synthesis and characterization of compound **7**, see Online Supplementary Materials.

(Butane-1,4-diyl)bis[(7-bromo-3,4-dihydroxy-1-naphthyl)(diphenyl)phosphonium] dibromide **8**. Dry hydrogen bromide (5-fold excess) was passed through a solution of bis-ylide **4** (0.50 g, 0.55 mmol) in 10 ml of benzene. The reaction mixture gradually produced dark-green precipitate, which was filtered off and dried at reduced pressure (12 Torr). The yield of compound **8** was 0.43 g (74%), mp 203–206 °C.

For characteristics of compound **8**, see Online Supplementary Materials.

(Butane-1,4-diyl)bis[(7-bromo-3,4-dihydroxy-1-naphthyl)(diphenyl)phosphonium] ditriflate **9**. To a solution of compound **4** (0.47 g, 0.52 mmol) in 5 ml of dichloromethane, a solution of 0.09 ml (1.04 mmol) of triflic acid was added dropwise under intense argon bubbling. After 3 days of standing colorless crystals of compound **9** were formed, which were filtered off and dried under reduced pressure (12 Torr), yield 0.49 g (61%, excluding two solvated hydroxonium triflate molecules), mp 128–131 °C. IR (ν/cm^{-1}): 3302 (OH), 1722, 1625, 1597 (C=C_{arom}), 1566, 1502, 1343 (C–F), 1224, 1168 (ν_{as} SO_2), 1115, 1078, 1028 (ν_{as} SO_2), 981, 960, 856, 818, 743, 690, 639, 601, 540, 479. ^1H NMR (DMSO-d_6) δ: 8.20 (dd, H^6, $^3J_{HCCH}$ 9.1 Hz, $^4J_{HCCCH}$ 1.9 Hz), 8.02–7.72 (m, H^{10}, H^{11}), 7.89 (m, H^{12}, $^3J_{HCCH}$ 7.2 Hz, $^5J_{PCCCCH}$ 1.6 Hz), 7.60 (dd, H^5, $^3J_{HCCH}$ 9.1 Hz, $^5J_{PCCCCH}$ 1.7 Hz), 7.42 (d, H^2, $^3J_{PCCH}$ 16.7 Hz), 7.37 (br. d, H^8, $^4J_{PCCCH}$ 1.2 Hz), 3.64 (m, H^{13}), 1.76 (m, H^{14}). ^{13}C NMR (DMSO-d_6) δ_C: 146.76 [m (d), C^4, $^3J_{HCCC}$ 5.6–5.8 Hz, $^4J_{PCCCC}$ 2.6 Hz], 140.58 [dd (d), C^3, $^3J_{PCCC}$ 17.6 Hz, $^2J_{HCC}$ 3.6 Hz], 135.17 [dt (br. s), C^{12}, $^1J_{HC}$ 170.0 Hz, $^3J_{HCCC}$ 5.6–6.5 Hz], 133.35 [ddd (d), C^{10}, $^1J_{HC}$ 169.2 Hz, $^2J_{PCC}$ 10.3 Hz, $^3J_{HCCC}$ 6.9 Hz], 130.70 [ddd (d), C^{11}, $^1J_{HC}$ 160.5 Hz, $^3J_{PCCC}$ 12.5 Hz, $^3J_{HCCC}$ 6.9 Hz], 130.07 [dd (d), C^2, $^1J_{HC}$ 160.7 Hz, $^2J_{PCC}$ 12.1 Hz], 129.88 [m (d), C^{8a}, $^2J_{PCC}$ 9.2 Hz, overlaps with C^{11} signal], 129.21 [dd (s), C^8, $^1J_{HC}$ 163.9 Hz, $^3J_{HCCC}$ 6.0 Hz], 126.33 [ddd (d), C^8, $^1J_{HC}$ 167.6 Hz, $^3J_{HCCC}$ 4.7–4.8 Hz, $^3J_{PCCC}$ 5.9 Hz], 125.66 [d (s), C^5, $^1J_{HC}$ 166.7 Hz], 125.41 [m (d), C^{4a}, $^3J_{PCCC}$ 12.1 Hz, overlaps with C^8 signal], 120.89 [q (q), C^{23}, $^1J_{FC}$ 321.0 Hz], 119.72 [ddt (d), C^9, $^1J_{PC}$ 85.8 Hz, $^3J_{HCCC}$ 7.1 Hz, $^2J_{HCC}$ 1.4–1.6 Hz], 119.70 [ddd (s), C^7, $^3J_{HCCC}$ 13.0 Hz, $^2J_{HCC}$ 5.9 Hz, $^2J_{HCC}$ 5.7 Hz], 99.28 [ddd (d), C^1, $^1J_{PC}$ 91.3 Hz, $^3J_{HCCC}$ 2.7–3.3 Hz, $^2J_{HCC}$ 1.2–1.4 Hz], 23.83 [tdm (d), C^{22}, $^1J_{HC}$ 132.2–136.5 Hz, $^2J_{PCC}$ 2.2 Hz], 21.76 [td (d), C^{21}, $^1J_{HC}$ 132.1–134.3 Hz, $^1J_{PC}$ 51.7 Hz]. ^{31}P / ^{31}P-{^1H} NMR ($CDCl_3$) δ_P: 21.2 [m (s)]. Found (%): Br, 10.51; P, 4.07, S 8.16. Calc. for $C_{52}H_{46}Br_2F_{12}O_{18}P_2S_4$ (%): Br, 10.41; P, 4.04; S 8.33. For more details, see Online Supplementary Materials.

(Pentane-1,5-diyl)bis[(7-bromo-3,4-dihydroxy-1-naphthyl)(diphenyl)phosphonium] ditriflate **10**. Yield 85%, mp 98–100 °C. For synthesis and characteristics of compound **10**, see Online Supplementary Materials.

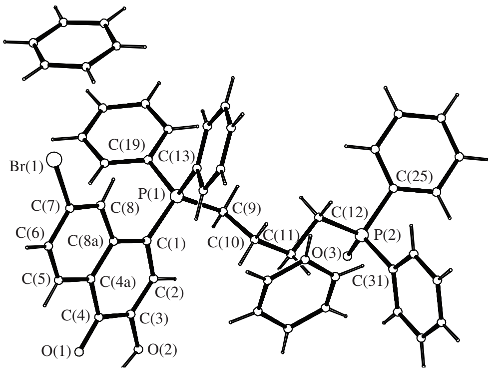


Figure 1 Molecular structure and atom-labeling scheme for compound **5** (solvate with three benzene molecules, one benzene molecule is omitted for clarity). Selected bond lengths (Å), bond and torsion angles (°): Br(1)–C(7) 1.912(4), P(1)–C(1) 1.760(4), P(1)–C(9) 1.814(3), P(1)–C(13) 1.813(4), P(2)–O(3) 1.482(2), C(2)–C(1) 1.424(5), C(2)–C(3) 1.359(5), O(2)–C(3) 1.402(5), C(4)–O(1) 1.286(5), C(4)–C(3) 1.412(5), C(1)–P(1)–C(9) 110.2(2), C(1)–C(2)–C(3) 123.2(4), C(4a)–C(8a)–C(1) 118.7(3), C(4)–C(4a)–C(8a) 122.1(4), O(1)–C(4)–C(3) 120.8(4), O(1)–C(4)–C(4a) 123.1(4), C(3)–C(4)–C(4a) 116.1(4), C(2)–C(1)–P(1) 118.3(3), C(8a)–C(1)–P(1) 125(2), O(2)–C(3)–C(4) 118.2(4), C(1)–P(1)–C(9) 110.18(18), O(3)–P(2)–C(16) 114.3(2), O(3)–P(2)–C(17) 112.2(2). For more data, see Online Supplementary Materials.

For compound **4**, the signal with δ_P 19.4 ppm in ^{31}P-{^1H} NMR spectrum is related to the ylide phosphorus atom. The electron impact mass spectrum (EI-MS) contains a peak of molecular ion with *m*/*z* 900.9. According to the ^{13}C-{^1H} NMR spectra the signal of C^1 atom is manifested in relatively high field (δ_C 122.36 ppm) that may indicate the here C-centred negative charge. The ^{31}P -{^1H} NMR spectrum of compound **5** contains two signals with δ_P 20.6 and 31.8 ppm with equal integral intensity corresponding to phosphonium and phosphine oxide functions.[27] In addition, its IR spectrum contains an intense absorption band of P=O bond. EI-MS of this compound contains peak of a molecular ion with *m*/*z* 677.0. The structure of compound **5** (as a solvate with three benzene molecules) was ultimately confirmed by XRD[‡] (Figure 1). Both phosphorus atoms have a distorted tetrahedral configuration and tetramethylene spacer is in a *gauche*-conformation along C(10)–C(11) bond.

The ^{31}P-{^1H} NMR spectrum of phosphino ylide **6** contains two signals of phosphonium and phosphine groupings (P^{IV}, δ_P 18.6 ppm and P^{III}, δ_P –15.6 ppm).

Further lengthening of the spacer by one methylene unit on moving to 1,5-bis(diphenylphosphino)pentane **3** allowed us to obtain the next bis-ylide **7**, whose content in the reaction mixture was about 100%.

Treatment of bis-ylides **4** and **7** with dry hydrogen bromide or triflic acid gave stable *P*,*P*′-bis(7-bromo-3,4-dihydroxy-1-naphthyl)-substituted phosphonium salts **8**–**10**[†] (Scheme 2). Compound **8** is characterized by a singlet at δ_P 22.2 ppm in the ^{31}P-{^1H} NMR spectrum. The broad absorption band at 3560–3564 cm^{-1} in the IR spectrum of salt **8** is related to the stretching vibrations of hydroxy groups. The signals of C^3 and C^4 atoms in the ^{13}C-{^1H} NMR spectrum of **8** manifest itself in the higher field (δ_C 140.31 and 146.71 ppm) than corresponding ones of ylide **4**. Upfield shift of the C^1 signal in compound **8** (from δ_C 122.36 to 97.97 ppm) points out the change of electronic situation at carbon atom (disappearing of the negative charge) and formation of phosphonium salt from ylide.

Bis-phosphonium ditriflate **9** was obtained after crystallization from dichloromethane and its structure was confirmed by XRD (Figure 2).[‡] The crystal of **9** represents a solvate with two hydroxonium triflate molecules. Note that tetramethylene chain has an almost ideal planar conformation distinct from the molecule of **5** (see Figure 1).

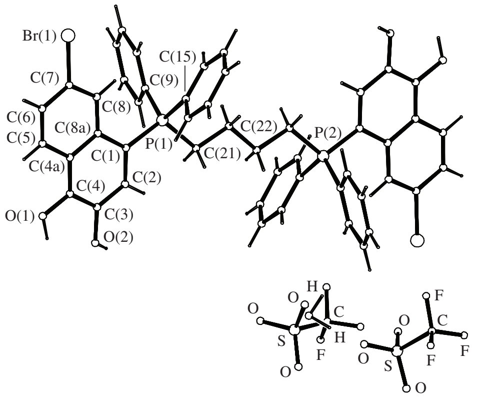


Figure 2 Molecular structure and atom-labeling scheme for compound **9** (two triflate anions and one hydroxonium cation are omitted for clarity). Selected bond lengths (Å), bond and torsion angles (°): Br(1)–C(7) 1.895(3), P(1)–C(1) 1.790(3), P(1)–C(9) 1.792(3), C(2)–C(1) 1.378(4), C(2)–C(3) 1.391(4), O(2)–C(3) 1.363(4), C(4)–O(1) 1.356(3), C(4)–C(3) 1.377(4), C(1)–P(1)–C(9) 109.4(1), C(1)–C(2)–C(3) 121.8(3), C(4a)–C(8a)–C(8) 17.7(3), C(4)–C(4a)–C(5) 121.7(3), C(3)–C(4)–P(1) 118.2(2), C(8a)–C(1)–P(1) 121.7(2), O(1)–C(4)–C(3) 120.4(3), O(1)–C(4)–C(4a) 18.4(3), O(2)–C(3)–C(4) 117.6(3), O(2)–C(3)–C(2) 123.1(3). For more data, see Online Supplementary Materials.

In conclusion, a facile and convenient synthesis of bis-phosphonium salts with various lengths of methylene spacer on the basis of the reaction of 6-bromo-1,2-naphthoquinone with tertiary diphosphines has been developed. Complexation reactions with *d*-metals as well as biological properties of compounds obtained will be reported elsewhere.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.11.019.

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[‡] X-ray diffraction analysis of crystals of compounds **5** and **9** was performed on a Bruker Smart APEX II CCD automatic diffractometer [graphite monochromator, λ(MoKα) = 0.71073 Å; ω-scanning, temperature 293 K]. All calculations were performed using APEX2[28] program.

Crystals of compound **5** are triclinic, $C_{38}H_{33}BrO_3P_2\cdot 3(C_6H_6)$, the experiment was performed in a glass capillary for the crystal instability. Unit cell parameters of a single crystal of **5**: a = 10.646(5), b = 12.013(5) and c = 17.478(9) Å, α = 83.918(8)°, β = 77.227(13)°, γ = 77.347(16)°, V = 2123.1(18) Å^3, Z = 2, space group $P\bar{1}$, M = 835.71, d_{calc} = 1.307(1) g cm^{-3}, μ(MoKα) = 1.085 mm^{-1}, $F(000)$ = 868, 2.00° ≤ θ ≤ 28.00°, R_{int} = 0.1451. 18711 reflections were measured, 9782 of them were independent, the number of observed reflections with $I > 2\sigma(I)$ were 3188. The final agreement factors are R = 0.0590, R_{w} = 0.0663, R_{all} = 0.0953, $R_{\mathrm{w\,all}}$ = 0.2100, GOF = 0.735, the number of refined parameters is 491.

Crystals of compound **9** are triclinic, $(C_{48}H_{40}Br_2O_4P_2)^{2+}\cdot 2(H_3O^+)\cdot 4(CF_3SO_3^-)$, dication $(C_{48}H_{40}Br_2O_4P_2)^{2+}$ is in a special position. Unit cell parameters of a single crystal of **9**: a = 9.3242(10), b = 11.4761(12) and c = 15.6236(16) Å, α = 76.264(1)°, β = 76.359(1)°, γ = 83.466(1)°, V = 1575.2(3) Å^3, Z = 1, space group $P\bar{1}$, M = 1536.91, d_{calc} = 1.620 g cm^{-3}, μ(MoKα) = 1.573 mm^{-1}, $F(000)$ = 774, 2.37° ≤ θ ≤ 24.6°, R_{int} = 0.0299. 17220 reflections were measured, 6787 of them were independent, the number of observed reflections with $I > 2\sigma(I)$ were 4493. The final agreement factors are R = 0.0494, R_{w} = 0.1227, R_{all} = 0.0830, $R_{\mathrm{w\,all}}$ = 0.1409, GOF = 1.014, the number of refined parameters is 434.

The structures were solved by direct method using SIR program[29] and refined by the full-matrix least-squares using SHELXL-97 program.[30] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed into the geometrically calculated positions and refined as riding atoms. The hydrogen atoms on the OH groups and oxonium cations were located from the difference Fourier synthesis and refined isotropically. All the figures and analysis of intermolecular interactions were performed using PLATON program.[31]

CCDC 818580 and 818558 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, 2011.