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Reactions of 2,2-dichloro(dibromo)-2-fluorobenzo[*d*]-1,3,2-dioxaphospholes with alk-1-ynes

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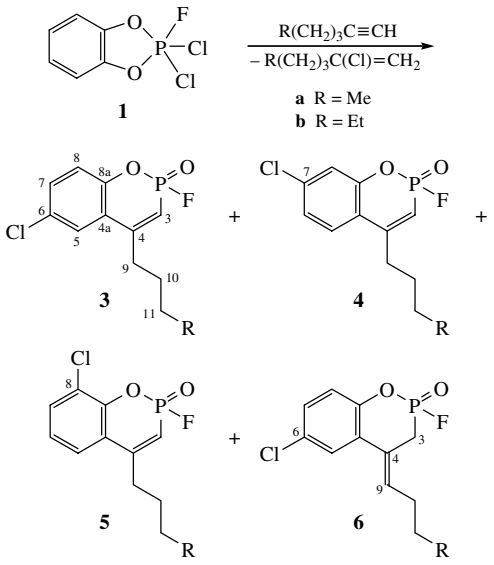
The title reactions are shown to yield mixtures of 4-alkyl-2-fluoro-2-oxobenzo[*e*]-1,2-oxaphosphorinine derivatives that are P-analogues of natural coumarin and α-chromen.

Previously, we found that 2,2,2-trihalobenzo[*d*]-1,3,2-dioxaphospholes react with arylacetylenes[1(*a*)] and hex-1-yne[1(*b*)] to give benzo[*e*]-1,2-oxaphosphorinine derivatives that are potential bioactive compounds, namely, P-analogues of coumarin and α-chromen.[2] Other multi-step methods for the synthesis of compounds of this type are also known.[3–6]

We studied the reactions of 2,2-dichloro(dibromo)-2-fluorobenzo[*d*]-1,3,2-dioxaphospholes **1**, **2** with hex-1-yne and hept-1-yne. We found that incorporation of a fluorine atom at the phosphorus atom (compound **1**) did not alter the direction of the reaction with hex-1-yne that again resulted in phosphorinine derivatives (Scheme 1). However, this was accompanied by partial modification of the benzo fragment chlorination regiochemistry to give three isomers **3a**, **4a** and **5a** in a 23:6:0.6 ratio. The structures of these compounds were confirmed by ^{1}H, ^{31}P and ^{13}C NMR spectroscopy.[†,‡] Thus, incorporation of a fluorine atom at P in phosphole **1** results in a small decrease in the phenylene fragment chlorination regioselectivity and in a change in the ratio between minor isomers formed. In this case, the fraction of the 7-chloro-substituted isomer is considerably

higher than that of the 8-chloro-substituted derivative. Furthermore, the distillation of reaction products results in an unusual allyl shift of the proton from C(9) to C(3) (compound **6a**). This compound is formed in trace amounts. It was detected by ^{1}H, ^{31}P and ^{13}C NMR spectroscopy. The reaction of phosphole **1** with hept-1-yne occurs similarly; the ratio of phosphorinines **3b**, **4b** and **5b** is 13:3.8:1.‡

The HCl that is evolved in the reactions partially adds to alk-1-ynes to give 2-chloroalk-1-enes, which can be easily separated by distillation *in vacuo*.



Scheme 1

Unlike the above cases, the reactions of dibromofluorophosphole **2** with alk-1-ynes are characterised by a decrease in the stereoselectivity of phenylene fragment bromination, and unsubstituted derivative **8** is formed in addition to brominated isomers **7**, **9** and **10** (Scheme 2). The ratio of phosphorinines **7a**, **8a**, **9a** and **10a** formed in the reaction of phosphole **2** with hex-1-yne§ amounts to 6:4:1:0.2. Under similar conditions, the reaction of phosphole **2** with hept-1-yne§ gives a mixture of phosphorinines **7b**, **8b**, **9b** and **10b** in a ratio of 10:5:3:1. Dilution of the reaction medium alters somewhat the ratio of compounds **7**–**10** (this issue requires a separate and more detailed study). The formation of a noticeable amount of unsubstituted compound **8** suggests that the ability of bromine to migrate to the phenylene fragment is smaller than that of chlorine. Note that no products of fluorine atom migration to the phenylene fragment are observed in reactions of phospholes **1**, **2** with alkynes. The compounds obtained could not be separated by distillation *in vacuo*; however, fractions were obtained that were enriched (up to 60–70%) in compounds **7** and **8** and contained phosphorinines **7**–**10** in different ratios. This allowed us to perform their full spectral identification. Compound **7a** was isolated by crystallisation from fractions that were most enriched with it. In certain fractions, 4-alkylidenophosphorinines **11** and **12** were detected by NMR spectroscopy.

The HBr and Br_2 evolved in the reactions are readily added to the starting alkynes to give a mixture of 2-bromoalk-2-enes, as well as *cis* and *trans* isomers of 1,2-dibromoalk-1-enes, which are easily separated by distillation *in vacuo*.

Hydrolysis of the resulting reaction mixtures and fractions isolated after distillation gives mixtures of the corresponding 2-hydroxyphosphorinines; fractional crystallisation of the latter

† Solvents and commercially available reagents were purified by conventional methods before use. All experiments were performed in an atmosphere of dry argon. Melting points are uncorrected. Measurements involved a Boetius melting point apparatus. NMR spectra were recorded on Bruker Avance-600 (600 MHz for ^{1}H; 150.9 MHz for ^{13}C, ^{13}C{^{1}H} or DEPT; 242.9 MHz for ^{31}P, ^{31}P{^{1}H}) and Bruker MSL-400 (400 MHz for ^{1}H) in $CDCl_3$ (20 °C) and [$^2H_6$]DMSO (40 °C). The δ_P values were determined relative to an external standard (H_3PO_4). The δ_C and δ_H values were determined relative to an internal standard (HMDS). EI mass spectra were obtained on a TRACE MS Finnigan MAT instrument; the energy of ionising electrons was 70 eV. The temperature of the ion source was 200 °C. The samples were introduced into the ion source using a direct inlet system. The temperature of the evaporator tube was adjusted in a programmed routine from 35 up to 190 °C. Mass-spectrometric data were processed using the Xcalibur program. 2,2-Dichloro(dibromo)-2-fluorobenzo[*d*]-1,3,2-dioxaphospholes were obtained using a published procedure.[8]

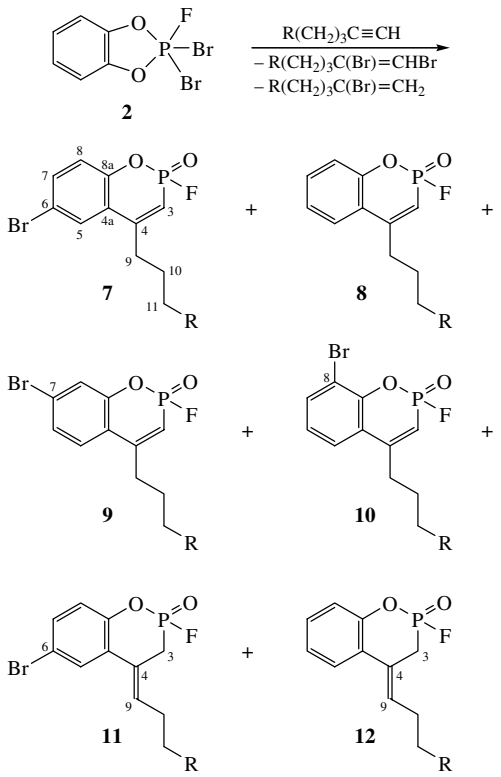
‡ *Reaction of phosphole* **1** *with hex-1-yne*. A solution of hex-1-yne (10 ml, 0.087 mol) in 15 ml of CH_2Cl_2 was added to a mixture of phosphole **1** (9.8 g, 0.043 mol) and 5 ml of CH_2Cl_2 (10–15 °C) with intensely bubbling argon. The reaction mixture was kept for 6 h and then evacuated (12 Torr, 130 °C) to give a light-brown glassy oil (a mixture of compounds **3a**–**5a** in a ratio of 23:6:0.6). A mixture of compounds **3a**–**6a** (bp 195–200 °C) was obtained after distillation *in vacuo* (0.1 Torr).

For **3a**: ^{31}P NMR ($CDCl_3$) δ_P (hereinafter, the multiplicity of the signal in the ^{31}P{^{1}H} NMR spectrum is given in parentheses): 7.0 [dd (d), $^1J_{PF}$ 1056.1 Hz, $^2J_{PCH}$ 18.0 Hz]. ^{13}C NMR ($CDCl_3$) δ_C: (hereinafter, the multiplicity of the signal in the ^{13}C{^{1}H} spectrum is given in parentheses) 106.60 [dddt (dd), C(3), $^1J_{PC(3)}$ 180.8, $^1J_{HC(3)}$ 167.0 Hz, $^2J_{FPC(3)}$ 28.5 Hz, $^3J_{HC(9)CC(3)}$ 5.6 Hz], 158.94 [m (s), C(4)], 122.08 [m (d), C(4a), $^3J_{PCCC(4a)}$ 17.9 Hz], 126.22 [br. dd (d), C(5), $^1J_{HC(5)}$ 165.1 Hz, $^3J_{HC(7)CC(5)}$ 6.0 Hz, $^4J_{POCCC(5)}$ 1.0 Hz], 130.11 [ddd (s), C(6), $^3J_{HC(8)CC(6)}$ 11.7 Hz, $^2J_{HC(7)C(6)}$ 4.5 Hz, $^2J_{HC(5)C(6)}$ 4.5 Hz], 131.70 [dd (s), C(7), $^1J_{HC(7)}$ 168.5 Hz, $^3J_{HC(5)CC(7)}$ 6.4 Hz], 120.85 [dd (d), C(8), $^1J_{HC(8)}$ 166.5 Hz, $^3J_{POCC(8)}$ 8.4 Hz], 149.30 [dddd (d), C(8a), $^3J_{HC(7)CC(8a)}$ 9.6–10.0 Hz, $^3J_{HC(5)CC(8a)}$ 9.6–10.0 Hz, $^2J_{POC(8a)}$ 8.3 Hz, $^2J_{HC(8)C(8a)}$ 4.8 Hz], 34.67 [br. tdm (d), C(9), $^1J_{HC(9)}$ 128.1 Hz, $^3J_{PCCC(9)}$ 18.9 Hz, $^3J_{HC(11)CC(9)}$ 5.0 Hz, $^2J_{HC(10)C(9)}$ 4.5–5.0 Hz], 29.77 [tm (s), C(10), $^1J_{HC(10)}$ 127.7 Hz, $^3J_{HC(12)CC(10)}$ 4.3–5.1 Hz, $^2J_{HC(9)C(10)}$ 4.3–5.1 Hz, $^2J_{HC(11)C(10)}$ 4.3–5.1 Hz], 22.23 [tm (s), C(11), $^1J_{HC(11)}$ 125.4 Hz, $^3J_{HC(9)CC(11)}$ 3.0–3.7 Hz, $^2J_{HC(10)C(11)}$ 3.0–3.7 Hz, $^2J_{HC(12)C(11)}$ 3.0–3.7 Hz], 13.73 [qm (s), C(12), $^1J_{HC(12)}$ 125.1 Hz, $^3J_{HC(10)CC(12)}$ 3.8–4.0 Hz, $^2J_{HC(11)C(12)}$ 3.2 Hz]. ^{1}H NMR ($CDCl_3$) δ_H: 6.04 [d, 1H, H(3), $^2J_{PCH}$ 17.8 Hz], 7.45 [d, 1H, H(5), $^4J_{H(7)CCCH(5)}$ 2.5 Hz], 7.28 [ddd, 1H, H(7), $^3J_{H(8)CCH(7)}$ 8.7 Hz, $^4J_{H(5)CCCH(7)}$ 2.5 Hz, $^5J_{POCCCH(7)}$ 1.5 Hz], 7.06 [d, 1H, H(8), $^3J_{H(7)CCH(8)}$ 8.7 Hz], 2.58–2.61 [m, 2H, C(9)H_2, AB-part of ABX_2-spectrum], 1.51 [m, 2H, C(10)H_2, $^3J_{HCCH}$ 7.6 Hz, $^3J_{HCCH}$ 7.5 Hz], 1.34 [m, 2H, C(11)H_2, $^3J_{HCCH}$ 7.4–7.5 Hz], 0.86 [t, 3H, C(12)H_3, $^3J_{H(11)CCH(12)}$ 7.3 Hz]. MS, *m*/*z* (hereinafter, the values of *m*/*z* are given for ions containing the most widespread isotopes): 277 (6.9), 276 (22.1), 275 (18.6), $[M + H]^+$, 274 (41.9) $[M]^{+\cdot}$, 240 (9.7), 239 (51.9) $[M - Cl]^+$, 234 (85.9), 234 (74.5), 232 (100.0) $[M - C_3H_6]^+$.

For **4a**: ^{31}P NMR ($CDCl_3$) δ_P: 7.3 [dd (d), $^1J_{PF}$ 1057.0 Hz, $^2J_{PCH}$ 18.2 Hz]. ^{13}C NMR ($CDCl_3$) δ_C: 105.40 [dddt (dd), C(3), $^1J_{PC(3)}$ 181.0 Hz, $^1J_{HC(3)}$ 167.0 Hz, $^2J_{FPC(3)}$ 28.3 Hz, $^3J_{HC(9)CC(3)}$ 5.5 Hz], 155.91 [m (s), C(4)], 119.45 [m (d), C(4a), $^3J_{PCCC(4a)}$ 18.2 Hz], 127.59 [dd (d), C(5), $^1J_{HC(5)}$ 162.6 Hz, $^4J_{POCCC(5)}$ 1.0 Hz], 125.05 [br. dd (d), C(6), $^1J_{HC(6)}$ 164.5 Hz, $^3J_{HC(8)CC(6)}$ 8.4 Hz, $^5J_{POCCCC(6)}$ 0.8 Hz], 137.31 [ddd (s), C(7), $^3J_{HC(5)CC(7)}$ 12.8 Hz, $^2J_{HCC(7)}$ 4.5 Hz, $^2J_{HCC(7)}$ 4.2 Hz], 119.68 [dddd (d), C(8), $^1J_{HC(8)}$ 169.2 Hz, $^3J_{POCC(8)}$ 8.7 Hz, $^3J_{HC(6)CC(8)}$ 5.6 Hz, $^4J_{HC(5)CCC(8)}$ 1.0 Hz], 151.13 [ddd (d), C(8a), $^3J_{HC(5)CC(8a)}$ 10.3 Hz, $^2J_{POC(8a)}$ 8.0 Hz, $^2J_{HC(8)C(8a)}$ 4.0 Hz], 34.80 [tdm (d), C(9), $^1J_{HC(9)}$ 128.0–129.0 Hz, $^3J_{PCCC(9)}$ 19.4 Hz], 29.95 [tm (s), C(10), $^1J_{HC(10)}$ 127.0–128.0 Hz], 22.28 [tm (s), C(11), $^1J_{HC(11)}$ 125.0–126.0 Hz], 13.73 [qm (s), C(12), $^1J_{HC(12)}$ 125.1 Hz, $^3J_{HC(10)CC(12)}$ 3.8–4.0 Hz, $^2J_{HC(11)C(12)}$ 3.8–4.0 Hz]. ^{1}H NMR ($CDCl_3$) δ_H: 6.05 [d, H(3), $^2J_{PCH}$ 18.0 Hz], 7.39 [br. d, H(5), $^3J_{H(6)CCH(5)}$ 8.6 Hz], 7.12 [dd, H(6), $^3J_{H(5)CCH(6)}$ 8.6 Hz, $^4J_{H(8)CCCH(6)}$ 2.1 Hz], 7.09 [d, H(8), $^4J_{H(6)CCCH(8)}$ 2.1 Hz].

The reaction mixture was dissolved in diethyl ether and hydrolysed with an excess of water. The white precipitate of 4-butyl-6-chloro-2-hydroxy-2-oxobenzo[*e*]-1,2-oxaphosphorinine **13a** was filtered off and recrystallised from dioxane, yield 52%, mp 132–135 °C. ^{1}H NMR (400 MHz, [$^2H_6$]DMSO) δ_H: 6.19 [d, 1H, H(3), $^2J_{PCH}$ 17.3 Hz], 7.62 [d, 1H, H(5), $^4J_{H(7)CCCH(5)}$ 2.5 Hz], 7.43 [ddd, 1H, H(7), $^3J_{H(8)CCH(7)}$ 8.7 Hz, $^4J_{H(5)CCCH(7)}$ 2.5 Hz, $^5J_{POCCCH(7)}$ 1.3 Hz], 7.20 [d, 1H, H(8), $^3J_{H(7)CCH(8)}$ 8.7 Hz], 2.64 [t, 2H, C(9)H_2, $^3J_{HCCH}$ 7.6 Hz], 1.50 [m, 2H, C(10)H_2, $^3J_{HCCH}$ 7.6 Hz, $^3J_{HCCH}$ 7.5 Hz], 1.38 [m, 2H, C(11)H_2, $^3J_{HCCH}$ 7.5–7.6 Hz], 0.92 [t, 3H, C(12)H_3, $^3J_{H(11)CCH(12)}$ 7.3 Hz]. IR (ν/cm^{-1}): 403, 437, 459, 488, 505, 522, 549, 594, 669, 723, 736, 776, 820, 840, 879, 904, 943, 994, 1029, 1064, 1084, 1118, 1135, 1180, 1234, 1248, 1268, 1312, 1377, 1421, 1463, 1554, 1602, 1644, 1894, 2265, 2670, 2725, 2851, 3046, 3437. Found (%): C, 52.91; H, 5.33; Cl, 13.19; P, 11.09. Calc. for $C_{12}H_{14}ClO_3P$ (%): C, 52.84; H, 5.14; Cl, 13.03; P, 11.38.

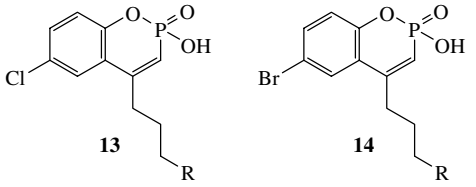
Spectral characteristics of compounds **5a** and **6a** as well as procedures for the reaction of phosphole **1** with hept-1-yne and spectral characteristics of compounds **3b**–**6b** and **13b** are available free *via* http://www.turpion.org/suppl/mc/2321/suppl2321.pdf as Supplementary Materials.



a R = Me
b R = Et

Scheme 2

gave 6-halo-substituted acids **13** and **14** (Scheme 3). These compounds are most readily crystallised from the reaction mixtures dissolved in diethyl ether.



a R = Me
b R = Et

Scheme 3

Thus, reactions of 2,2-dichloro(dibromo)-2-fluorobenzo[*d*]-1,3,2-dioxaphospholes with alkynes allow hardly accessible derivatives of 6-chloro(bromo)-substituted benzo[*e*]-1,2-oxaphosphorinines to be obtained in one stage. Specific features of the processes involved include an overall decrease in the halogenation regioselectivity and preferential formation of 6-halo-substituted benzo[*e*]-1,2-oxaphosphorinines. The reaction with 2,2-dibromo-2-fluorobenzo[*d*]-1,3,2-dioxaphosphole results in benzo[*e*]-1,2-oxaphosphorinines that contain no halogen at the phenylene fragment.

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§ *Reaction of phosphole* **2** *with hex-1-yne*. A solution of hex-1-yne (13.5 ml, 0.117 mol) in 10 ml of CH_2Cl_2 was added to a solution of phosphole **1** (18.66 g, 0.0587 mol) in 120 ml of CH_2Cl_2 (10–20 °C). The reaction mixture was kept for 6 h and then evacuated (12 Torr, 130 °C) to give a dark-brown glassy oil (a mixture of compounds **7a**–**10a** in a ratio of 6:4:1:0.2). Two main fractions of the mixture of compounds **7a**–**12a** were obtained after distillation *in vacuo* (0.1 Torr): i, bp 180–187 °C (0.1 Torr) (a mixture of **7a**–**11a** in the ratio of 5:5:1:0.3:0.3), and ii, bp 192–197 °C (0.1 Torr) (a mixture of **7a**–**11a** in the ratio of 5:1:1:0.3:0.3).

For **7a**: ^{31}P NMR ($CDCl_3$) δ_P: 6.9 [dd (d), $^1J_{PF}$ 1059.3 Hz, $^2J_{PCH}$ 17.9 Hz]. ^{13}C NMR ($CDCl_3$) δ_C: 107.04 [dddt (dd), C(3), $^1J_{PC(3)}$ 179.3 Hz, $^1J_{HC(3)}$ 168.0 Hz, $^2J_{FPC(3)}$ 28.7 Hz, $^3J_{HC(9)CC(3)}$ 5.5 Hz], 158.54 [m (s), C(4)], 122.71 [m (d), C(4a), $^3J_{PCCC(4a)}$ 18.2 Hz], 129.19 [dd (d), C(5), $^1J_{HC(5)}$ 168.0 Hz, $^3J_{HC(7)CC(5)}$ 6.1 Hz], 117.30 [ddd (s), C(6), $^3J_{HC(8)CC(6)}$ 11.6 Hz, $^2J_{HC(7)C(6)}$ 3.6 Hz, $^2J_{HC(5)C(6)}$ 4.5 Hz], 134.46 [dd (s), C(7), $^1J_{HC(7)}$ 169.6 Hz, $^3J_{HC(5)CC(7)}$ 6.8 Hz], 121.13 [dd (d), C(8), $^1J_{HC(8)}$ 167.0 Hz, $^3J_{POCC(8)}$ 8.3 Hz], 149.88 [dddd (d), C(8a), $^3J_{HC(7)CC(8a)}$ 9.0–10.0 Hz, $^3J_{HC(5)CC(8a)}$ 9.0–10.0 Hz, $^2J_{POC(8a)}$ 8.1 Hz, $^2J_{HC(8)C(8a)}$ 4.0 Hz], 33.90 [tdm (d), C(9), $^1J_{HC(9)}$ 128.1 Hz, $^3J_{PCCC(9)}$ 18.9 Hz, $^3J_{HC(11)CC(9)}$ 5.3 Hz, $^2J_{HC(10)C(9)}$ 3.0–4.0 Hz, $^2J_{HC(10)C(9)}$ 3.0–4.0 Hz], 29.36 [tm (s), C(10), $^1J_{HC(10)}$ 127.7 Hz, $^3J_{HC(12)CC(10)}$ 4.8–5.3 Hz, $^2J_{HC(9)C(10)}$ 4.8–5.3 Hz], 22.17 [tm (s), C(11), $^1J_{HC(11)}$ 126.3 Hz, $^3J_{HC(9)CC(11)}$ 3.3–4.2 Hz, $^2J_{HC(10)C(11)}$ 3.3–4.2 Hz], 13.73 [qm (s), C(12), $^1J_{HC(12)}$ 125.0 Hz, $^3J_{HC(10)CC(12)}$ 3.5–4.2 Hz, $^2J_{HC(11)C(12)}$ 3.5–4.2 Hz]. ^{1}H NMR ($CDCl_3$) δ_H: 6.05 [d, 1H, H(3), $^2J_{PCH}$ 17.8 Hz], 7.60 [d, 1H, H(5), $^4J_{H(7)CCCH(5)}$ 2.4 Hz], 7.42 [ddd, 1H, H(7), $^3J_{H(8)CCH(7)}$ 8.7 Hz, $^4J_{H(5)CCCH(7)}$ 2.4 Hz, $^5J_{POCCCH(7)}$ 1.6 Hz], 7.00 [d, 1H, H(8), $^3J_{H(7)CCH(8)}$ 8.7 Hz], 2.59–2.63 [m, 2H, H(9), AB-part of ABX_2-spectrum], 1.50 [m, 2H, H(10), $^3J_{HCCH}$ 7.3 Hz], 1.32 [m, 2H, H(11), $^3J_{HCCH}$ 7.3–7.4 Hz], 0.85 [m, 3H, H(12), $^3J_{H(11)CCH(12)}$ 7.4 Hz].

For **8a**: ^{31}P NMR ($CDCl_3$) δ_P: 7.7 [dd (d), $^1J_{PF}$ 1055.0 Hz, $^2J_{PCH}$ 18.3 Hz]. ^{13}C NMR ($CDCl_3$) δ_C: 105.24 [dddt (dd), C(3), $^1J_{PC(3)}$ 180.2 Hz, $^1J_{HC(3)}$ 166.7 Hz, $^2J_{FPC(3)}$ 28.5 Hz, $^3J_{HC(9)CC(3)}$ 5.6 Hz], 160.23 [m (s), C(4)], 120.62 [m (d), C(4a), $^3J_{PCCC(4a)}$ 18.2 Hz], 126.53 [dd (s), C(5), $^1J_{HC(5)}$ 160.3 Hz, $^3J_{HC(7)CC(5)}$ 8.4 Hz], 124.74 [dd (s), C(6), $^1J_{HC(6)}$ 162.8 Hz, $^3J_{HC(8)CC(6)}$ 7.9 Hz], 134.61 [dd (s), C(7), $^1J_{HC(7)}$ 169.5 Hz, $^3J_{HC(5)CC(7)}$ 6.6 Hz], 119.13 [dd (s), C(8), $^1J_{HC(8)}$ 164.5 Hz, $^3J_{POCC(8)}$ 8.4 Hz, $^3J_{HC(6)CC(8)}$ 8.1 Hz], 150.80 [m (d), $^2J_{POC(8a)}$ 8.6 Hz, $^2J_{HC(8)C(8a)}$ 4.0 Hz], 34.77 [mdm (d), C(9), $^1J_{HC(9)}$ 127.9 Hz, $^3J_{PCCC(9)}$ 19.7 Hz, $^3J_{HC(3)CC(9)}$ 5.3 Hz, $^2J_{HC(10)C(9)}$ 4.4 Hz, $^2J_{HC(10)C(9)}$ 4.4 Hz], 30.00 [tm (s), C(10), $^1J_{HC(10)}$ 126.7 Hz, $^3J_{HC(12)CC(10)}$ 4.8–5.0 Hz, $^2J_{HC(9)C(10)}$ 4.8–5.0 Hz], 22.25 [tm (s), C(11), $^1J_{HC(11)}$ 125.1 Hz, $^3J_{HC(9)CC(11)}$ 3.8–4.2 Hz, $^2J_{HC(10)C(11)}$ 3.8–4.2 Hz], 13.68 [qm (s), C(12), $^1J_{HC(12)}$ 125.1 Hz, $^3J_{HC(10)CC(12)}$ 3.8–4.2 Hz, $^2J_{HC(11)C(12)}$ 3.8–4.2 Hz]. ^{1}H NMR ($CDCl_3$) δ_H: 5.98 [d, H(3), $^2J_{PCH}$ 18.4 Hz], 7.51 [dd, H(5), $^3J_{HC(6)CH(5)}$ 8.0 Hz, $^4J_{HC(7)CCH(5)}$ 1.5 Hz], 7.16 [ddd, H(6), $^3J_{H(7)CCH(6)}$ 7.4 Hz, $^3J_{H(5)CCH(6)}$ 8.0 Hz, $^4J_{H(8)CCCH(6)}$ 1.2 Hz], 7.33 [dddd, H(7), $^3J_{H(8)CCH(7)}$ 8.0 Hz, $^3J_{H(6)CCH(7)}$ 7.4 Hz, $^4J_{H(5)CCCH(7)}$ 1.5 Hz, $^5J_{POCCCH(7)}$ 1.5 Hz], 7.09 [dd, H(8), $^3J_{H(7)CCH(8)}$ 8.2 Hz, $^4J_{H(6)CCCH(8)}$ 1.2 Hz], 2.59–2.63 [m, H(9), AB-part of ABX_2-spectrum], 1.51 [m, H(10), $^3J_{HCCH}$ 7.2–7.4 Hz], 1.34 [m, H(11), $^3J_{HCCH}$ 7.3–7.4 Hz], 0.86 [t, H(12), $^3J_{H(11)CCH(12)}$ 7.3 Hz].

Spectral characteristics of compounds **9a**–**12a** as well as procedures for the reaction of phosphole **2** with hept-1-yne and spectral characteristics of compounds **7b**–**12b** and **14b** are available free *via* http://www.turpion.org/suppl/mc/2321/suppl2321.pdf as Supplementary materials.