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Synthesis and crystal structure of 5-carbaphosphatranes containing a four-membered cycle

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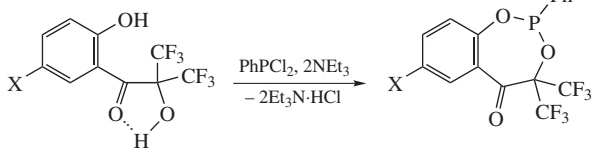
4,4-Bis(trifluoromethyl)-4,5-dihydro-2-phenylbenzo[*e*]- and 4,4-bis(trifluoromethyl)-4,5-dihydro-2-phenyl-(4′-chlorobenzo)[*e*]-1,3,2-dioxaphosphepin-5-ones react with hexafluoroacetone to form unusual propeller type structures – 3,3,10,10-tetrakis-(trifluoromethyl)-1-phenyl-6,7-benzo- and 3,3,10,10-tetrakis(trifluoromethyl)-1-phenyl-6,7-(4′-chlorobenzo)-2,4,8,9-tetraoxa-1-phosphatricyclo[3.3.2.0^{1,5}]decenes (5-carbaphosphatrane derivatives), the structure of which has been determined by NMR spectroscopy and single crystal X-ray diffraction analysis.

Phosphorus(III) derivatives containing a functional substituent, such as NCO, NCS, OC(O)R, C(R′)=CR$_2$ and C≡CR, are convenient precursors for various P-heterocyclic systems.[1–3] They include an activated multiple bond and easily react with unsaturated compounds, such as aldehydes, ketones, alkenes and imines *via* an initial nucleophilic attack of the phosphorus atom followed by a transfer of the reactive centre on the multiple bond of exocyclic substituent. At the same time, various rearrangements can take place.[1,2]

Here we have shown for the first time that P-heterocycles, bearing an endocyclic carbonyl group in the γ-position to phosphorus, can be used for the synthesis of the new heterocyclic system. We have synthesized new seven-membered heterocycles **3**, **4** (Scheme 1) by the phosphorylation of fluorinated hydroxyketones **1**, **2**, obtained according to published data,[4] with dichlorophenylphosphine in the presence of triethylamine. These unusual compounds contain two reactive centres: a nucleophilic phosphorus atom and an electrophilic carbonyl group. In spite of this fact, they are stable at 20 °C. NMR spectra confirmed their structure.

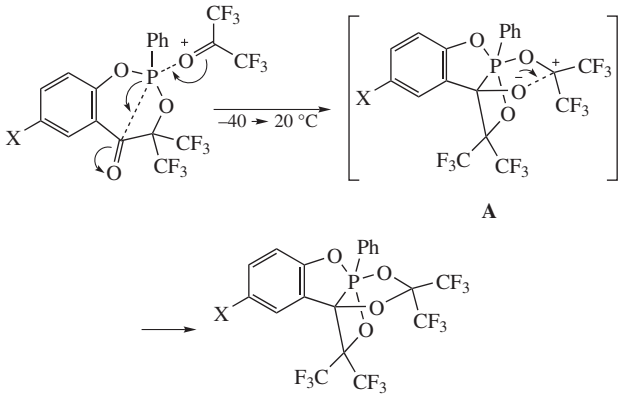


1 X = H
2 X = Cl

3 X = H
4 X = Cl

Scheme 1

The reaction of benzophosphepin-5-ones **3**, **4** with hexafluoroacetone leads to the formation of propeller-like pentacoordinated phosphorus species **5**, **6** bearing two five-membered and one four-membered rings, which are annelated along the common phosphorus–carbon bond (Scheme 2). Derivatives **5**, **6** are a new class of 5-carbaphosphatranes. Compounds containing only five- and six-membered cycles are known among them.[5–9] The reaction is likely to include an intramolecular attack of phosphorus on the endocyclic carbonyl group and a simultaneous interaction of the hexafluoroacetone carbonyl oxygen with phosphorus leading to the formation of intermediate **A**. Further attack of oxygen on carbon gives reaction products **5**, **6**.



A

5 X = H
6 X = Cl

Scheme 2

The structure of compounds **5**, **6** was established by a variety of correlation NMR methods (2D COSY-gp, 2D HSQC-gp, 2D HMBC-gp).† Analysis of these compounds was carried out in the identical way therefore only for **5** detailed description will be given.

The ^{1}H NMR spectrum of **5** consists of several signals of aromatic protons. Two groups of protons of benzo moiety and phenyl group uniquely stand out in the spectrum 2D COSY. The ^{13}C NMR chemical shifts of all hydrogenated carbons could be assigned unambiguously by the 2D HSQC spectrum.

The structures of the fragments of **5** were conclusively established based on HMBC correlations (Figure 1). The most important ones are between the protons at δ 7.53 (H^{11}), 7.16 (H^{14}) and the carbon resonance at δ 91.16 (C^5); the protons at δ 7.53 (H^{11}) and 7.45 (H^{13}) and the carbon resonance at δ 154.28 (C^7); the protons at δ 7.53 (H^{17}/H^{19}), and the carbon resonance at δ 133.86 (C^{15}).

Unfortunately, the rest of the carbons (C^{3,10}, C$^{21\text{-}24}$) cannot be assigned directly (non empirically) by 2D correlation techniques because these atoms are far away from the hydrogens and therefore there are no notable long-range spin-spin couplings to produce cross-peaks on these spectra. If to take into account that there are two electronegative oxygen atoms near to the C^3 and

only one in vicinity of C^{10}, the first multiplet at δ_C 96.49 can be assigned to C^3, while the second one at 80.83 ppm corresponds to C^{10}. Finally, there are almost no empirical rules to assign CF_3 groups resonating at δ_C 120.96, 120.23, 119.71 and 119.51 ppm.

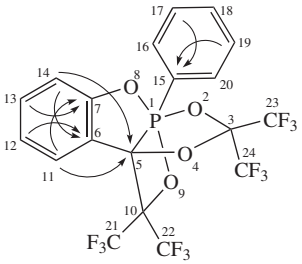


Figure 1 HMBC correlations for molecule of **5**.

The structure of compounds **5**, **6** was confirmed by single crystal X-ray diffraction (Figures 2 and 3).‡ The phosphorus atom has a nearly regular trigonal bipyramidal configuration in both molecules. The surprising feature of the structures of **5**, **6** is the apical location of two phosphorus–carbon bonds [$\angle C^5P^1C^{15}$ 171.7(2)° (**5**), 171.3(2)° (**6**)] and three equatorial phosphorus–oxygen bonds [$\angle O^2P^1O^9 + \angle O^2P^1O^8 + \angle O^8P^1O^9 = 358.5(1)°$ (**5**), 358.2(2)° (**6**); $\angle O^2P^1C^5$, $\angle O^8P^1C^5$, $\angle O^9P^1C^5$, $\angle O^2P^1C^{15}$, $\angle O^8P^1C^{15}$, $\angle O^9P^1C^{15} = 77.5(2)–95.8(2)°$ (**5**, **6**)]. The obtained equatorial phosphorus–oxygen bond lengths are within 1.623(2)–1.670(3) Å and agree closely with known values [1.661(2)–1.667(2) Å].[10–13] This molecule is a first example of the trigonal bipyramidal structure with three apical carbon – equatorial oxygen rings (one four-membered cycle and two five-membered ones). The apical P^1–C^5 and P^1–C^{15} bond lengths are rather distinguished [1.879(4) and 1.804(4) Å for (**5**), 1.880(4) and 1.808(4) Å for (**6**), respectively]. It is interesting to note that the apical P^1–C^{15} bond length is shorter than apical and equatorial ones in related structures of **7**–**9** [$(P–C)_{eq}$ 1.806(4)–1.825(2) Å, $(P–C)_{ax}$ 1.860(4)–1.872(2) Å] characterized by K.-Y. Akiba.[11–18] To

† *3,3,10,10-Tetrakis(trifluoromethyl)-1-phenyl-6,7-benzo-2,4,8,9-tetraoxa-1-phosphatricyclo[3.3.2.0^{1,5}]decene* **5**. Hexafluoroacetone (4.2 g, 0.25 mol) was condensed to the mixture of phosphonite **3** (4.88 g, 0.012 mol) and CH_2Cl_2 (30 ml) in a dry argon atmosphere at –45 °C. The reaction mixture was heated to 20 °C for 6 h. Solvent was removed in a vacuum, and the residue (yellow oil) was dissolved in CH_2Cl_2–pentane (5:1). The obtained solution was kept for 6 days under conditions of the slow solvent graduation. Compound **5** was obtained as a crystalline solid. Yield 55%, mp 107 °C. IR (Nujol, ν/cm^{-1}): 1464, 1376, 1292, 1104, 1056, 980, 944, 904, 848, 808, 760, 720. ^{19}F NMR ($CDCl_3$) δ_F: –80.89 (qm, $C^3CF_3^A$, $^4J_{F^BCCCF^A}$ 10.3 Hz, $^4J_{POCCF^A}$ 2.3 Hz, $^7J_{F^XCCOCCCF^A}$ 2.0 Hz, $^7J_{F^YCCOCCCF^A}$ 2.0 Hz), –78.55 (br. m, $C^3CF_3^B$, $^4J_{F^ACCCF^B}$ 10.3 Hz, $^4J_{POCCF^B}$ 17.9 Hz, $^7J_{F^YCCOCCCF^B}$ 5.3 Hz, $^7J_{F^XCCOCCCF^B}$ 2.0 Hz), –74.13 (br. qm, $C^{10}CF_3^X$, $^4J_{F^YCCCF^X}$ 12.0 Hz, $^4J_{POCCF^X}$ 2.3 Hz, $^7J_{F^ACCOCCCF^X}$ 2.0–2.3 Hz, $^7J_{F^BCCOCCCF^X}$ 2.0–2.3 Hz), –71.51 (m, $C^{10}CF_3^Y$, $^4J_{F^XCCCF^Y}$ 12.0 Hz, $^4J_{POCCF^Y}$ 17.5 Hz, $^7J_{F^BCCOCCCF^Y}$ 5.0–5.3 Hz, $^7J_{F^ACCOCCCF^Y}$ 2.0 Hz). ^{1}H NMR, δ: 7.16 (br. d, 1H, H^{14}, $^3J_{H^{13}CCH^{14}}$ 8.2 Hz), 7.23 (dddd, 1H, H^{12}, $^3J_{H^{13}CCH^{12}}$ 7.8 Hz, $^3J_{H^{11}CCH^{12}}$ 7.6 Hz, $^4J_{H^{14}CCCH^{12}}$ 1.6 Hz, $^5J_{PCCCCH^{12}}$ 0.8 Hz), 7.46 (ddd, 1H, H^{13}, $^3J_{H^{14}CCH^{13}}$ 8.2 Hz, $^3J_{H^{12}CCH^{13}}$ 7.8 Hz, $^4J_{H^{11}CCCH^{13}}$ 2.0 Hz), 7.54 (m, 3H, H^{11}, H^{17}), 7.60 (m, 1H, H^{18}, $^3J_{H^{17}CCH^{18}}$ 7.3 Hz, $^4J_{H^{16}CCCH^{18}}$ 1.8 Hz), 8.01 (m, 2H, H^{16}, $^3J_{PCCH^{16}}$ 16.5 Hz, $^3J_{H^{17}CCH^{16}}$ 7.2 Hz). ^{13}C NMR (here and further a multiplicity of the signal in ^{13}C-{^{1}H} spectrum is given in brackets): 96.49 [sept. d (sept. d), C^3, $^2J_{FCC^3}$ 35.1 Hz, $^2J_{POC^3}$ 7.5 Hz], 91.16 [br. d (br. d), C^5, $^1J_{PC^5}$ 110.5 Hz], 123.41 [m (d), C^6, $^2J_{PC^5C^6}$ 4.8 Hz], 154.28 [m (d), C^7, $^2J_{POC^7}$ 9.6 Hz, $^3J_{HC^{11}CC^7}$ 9.8–10.7 Hz, $^3J_{HC^{13}CC^7}$ 9.8–10.7 Hz], 80.83 [sept. d (sept. d), C^{10}, $^2J_{FCC^{10}}$ 31.2 Hz, $^2J_{PCC^{10}}$ 19.2 Hz], 127.39 [ddd (d), C^{11}, $^1J_{HC^{11}}$ 162.8 Hz, $^3J_{PCCC^{11}}$ 18.6 Hz, $^2J_{HC^{13}CC^{11}}$ 8.4 Hz], 124.85 [dd (s), C^{12}, $^1J_{HC^{12}}$ 162.2 Hz, $^3J_{HC^{14}CC^{12}}$ 7.2 Hz], 132.37 [dd (s), C^{13}, $^1J_{HC^{13}}$ 161.6 Hz, $^3J_{HC^{11}CC^{13}}$ 8.4 Hz], 113.35 [ddd (d), C^{14}, $^1J_{HC^{14}}$ 165.2 Hz, $^3J_{POCC^{14}}$ 12.8 Hz, $^3J_{HC^{12}CC^{14}}$ 7.2 Hz], 133.87 [dt (d), C^{15}, $^1J_{PC^{15}}$ 233.1 Hz, $^3J_{HC^{17}CC^{15}}$ 8.8 Hz], 131.14 [dddd (d), C^{16}, C^{20}, $^1J_{HC^{16}}$ 162.8 Hz, $^2J_{PC^{15}C^{16}}$ 11.4 Hz, $^3J_{HC^{18}CC^{16}}$ 7.2 Hz, $^3J_{HC^{20}CC^{16}}$ 7.2 Hz], 128.54 [ddd (d), C^{17}, C^{19}, $^1J_{HC^{17}}$ 162.2 Hz, $^3J_{PCCC^{17}}$ 18.6 Hz, $^3J_{HC^{19}CC^{17}}$ 7.6 Hz], 132.60 [dtd (d), C^{18}, $^1J_{HC^{18}}$ 161.6 Hz, $^3J_{HC^{16}CC^{18}}$ 7.2 Hz, $^4J_{PCCCC^{18}}$ 3.6 Hz], 119. 51 [q (q), CF_3, $^1J_{FC}$ 290.2 Hz], 119.69 [qd (qd), CF_3, $^1J_{FC}$ 288.4 Hz, $^3J_{PC}$ 4.5 Hz], 120.24 [qd (qd), CF_3, $^1J_{FC}$ 285.3 Hz, $^3J_{PC}$ 12.0 Hz], 120.96 [qd (qd), CF_3, $^1J_{FC}$ 286.5 Hz, $^3J_{PC}$ 8.1 Hz]. ^{31}P-{^{1}H} NMR (121.42 MHz, $CDCl_3$) δ_P: 9.0 (br. m). MS, *m*/*z* (the values of *m*/*z* are given for ions containing the most widespread isotopes): 560 ($C_{19}H_9F_{12}O_4P$) $[M]^{+\cdot}$, 541 [M – F], 491 [M – CF_3], 394 [M – $(CF_3)_2CO$], 228 [M – 2$(CF_3)_2CO$], 166 [$(CF_3)_2CO$], 77 [Ph], 69 [CF_3].

3,3,10,10-Tetrakis(trifluoromethyl)-1-phenyl-6,7-(4'-chlorobenzo)-2,4,8,9-tetraoxa-1-phosphatricyclo[3.3.2.0^{1,5}]decene **6** was obtained similar to compound **5** from phosphonite **4** and hexafluoroacetone. Yield 77%, mp 91 °C. IR (ν/cm^{-1}): 2954, 2924, 2854, 1611, 1466, 1377, 1302, 1237, 1220, 1174, 1149, 1123, 1110, 1054, 1025, 985, 970, 955, 910, 890, 858, 823, 817, 795, 762, 754, 731, 718, 688. ^{1}H NMR (600 MHz, [$^2H_6$]acetone) δ: 7.38 (d, H^{14}, $^3J_{H^{13}H^{14}}$ 8.7 Hz), 7.56 (m, H^{17}, $^3J_{H^{18}H^{17}}$ 7.4–7.6 Hz, $^3J_{H^{16}H^{17}}$ 7.4–7.6 Hz, $^4J_{PCCCH^{17}}$ 6.5–6.6 Hz), 7.61 (dd, H^{13}, $^3J_{H^{14}H^{13}}$ 8.7 Hz, $^4J_{H^{11}CCCH^{13}}$ 2.4 Hz), 7.63 (tdt, H^{18}, $^3J_{H^{17}H^{18}}$ 7.4–7.6 Hz, $^5J_{PCCCCH^{18}}$ 2.0 Hz, $^4J_{H^{16}CCCH^{18}}$ 1.2 Hz), 7.72 (br. s, H^{11}), 7.96 (m, H^{16}, $^3J_{PCCH^{16}}$ 16.6 Hz, $^3J_{H^{17}H^{16}}$ 7.4–7.6 Hz). ^{19}F NMR ([$^2H_6$]acetone) δ: –74.29 (m, CF_3), –76.78 (br. q, CF_3, $^4J_{FF}$ 9.4 Hz), –81.25 (m, CF_3), –83.57 (br. q, CF_3, $^4J_{FF}$ 9.4 Hz). ^{13}C NMR ([$^2H_6$]acetone) δ: 96.65 [sept. d (sept. d), C^3, $^2J_{FCC^3}$ 35.4 Hz, $^2J_{POC^3}$ 7.2 Hz], 91.58 [br. d (br. d), C^5, $^1J_{PC^5}$ 109.0 Hz], 124.94 [br. dd (d), C^6, $^2J_{PC^5C^6}$ 6.2 Hz, $^3J_{HC^{14}CC^6}$ 6.5–7.0 Hz], 153.07 [m (d), C^7, $^2J_{POC^7}$ 9.4 Hz], 80.92 [sept. d (sept. d), C^{10}, $^2J_{FCC^{10}}$ 30.2 Hz, $^2J_{PCC^{10}}$ 18.2 Hz], 127.51 [ddd (d), C^{11}, $^1J_{HC^{11}}$ 169.7 Hz, $^3J_{PCCC^{11}}$ 19.0 Hz, $^2J_{HC^{13}CC^{11}}$ 6.0 Hz], 130.30 [ddd (s), C^{12}, $^3J_{HC^{14}CC^{12}}$ 7.2 Hz, $^2J_{H^{11}C^{12}}$ 4.0–4.1 Hz, $^2J_{H^{13}C^{12}}$ 4.0–4.1 Hz], 133.57 [dd (s), C^{13}, $^1J_{HC^{13}}$ 168.5 Hz, $^3J_{HC^{11}CC^{13}}$ 5.6 Hz], 115.81 [dd (d), C^{14}, $^1J_{HC^{14}}$ 169.9 Hz, $^3J_{POCC^{14}}$ 11.6 Hz], 133.25 [dt (d), C^{15}, $^1J_{PC^{15}}$ 231.9 Hz, $^3J_{HC^{17}CC^{15}}$ 8.0 Hz], 131.27 [ddm (d), C^{16}, C^{20}, $^1J_{HC^{16}}$ 163.5 Hz, $^2J_{PC^{15}C^{16}}$ 11.8 Hz, $^3J_{HCCC^{16}}$ 6.9 Hz, $^3J_{HCCC^{16}}$ 7.1 Hz, $^2J_{HCC^{16}}$ 2.1 Hz, $^4J_{HCCCC^{16}}$ 1.4 Hz], 129.17 [ddd (d), C^{17}, C^{19}, $^1J_{HC^{17}}$ 163.1 Hz, $^3J_{PCCC^{17}}$ 18.8 Hz, $^3J_{HC^{19}CC^{17}}$ 7.4 Hz], 132.97 [dtdd (d), C^{18}, $^1J_{HC^{18}}$ 162.4 Hz, $^3J_{HC^{16}CC^{18}}$ 7.4 Hz, $^4J_{PCCCC^{18}}$ 3.3 Hz, $^2J_{HC^{17}C^{18}}$ 1.2 Hz], 119.77 [q (q), $C^{10}CF_3$, $^1J_{FC}$ 289.8 Hz], 119.95 [qd (qd), $C^{10}CF_3$, $^1J_{FC}$ 287.2 Hz, $^3J_{PCC^{10}C}$ 5.2 Hz], 120.46 [qd (qd), C^3CF_3, $^1J_{FC}$ 285.3 Hz, $^3J_{PC}$ 11.6 Hz], 121.19 [qd (qd), C^3CF_3, $^1J_{FC}$ 285.8 Hz, $^3J_{PC}$ 8.5 Hz]. ^{31}P-{^{1}H} NMR (121.42 MHz, [$^2H_6$]acetone) δ_P: 11.0 (br. m). MS, *m*/*z* (the values of *m*/*z* are given for ions containing the most widespread isotopes): 594 ($C_{19}H_8ClF_{12}O_4P$) $[M]^{+\cdot}$, 575 [M – F], 525 [M – CF_3], 428 [M – $(CF_3)_2CO$], 262 [M – 2$(CF_3)_2CO$], 166 [$(CF_3)_2CO$], 77 [Ph], 69 [CF_3].

‡ *X-ray crystallography*. The crystal data for compounds **5** and **6** were collected on the CAD 4 Enraf-Nonius diffractometer (graphite monochromated CuKα radiation, λ = 1.54184 Å).[19] The stability of the crystal and experimental conditions were being checked every 2 h using three control reflections, while the orientation was being monitored every 200 reflections by centering two standards. No significant decay was observed. Corrections for Lorentz and polarization effects and absorption correction were applied. The structure was solved by direct methods using SIR.[20] Full-matrix least-squares refinement on F^2 was performed using SHELXL-97[21] and WinGX[22] software packages with anisotropic displacements for non-hydrogen atoms. All hydrogen atoms were placed in idealized positions and refined by using the riding model. Illustrations were made using Platon.[23]

Crystallographic data for **5**: $C_{19}H_9F_{12}O_4P$, M = 560.23, light-yellow prism of dimensions 0.4×0.4×0.3 mm, triclinic, space group $P\bar{1}$, at 293 K, a = 9.551(5), b = 10.242(9) and c = 10.601(6) Å, α = 88.14(5)°, β = 84.16(5)°, γ = 85.00(6)°, V = 1027.4(12) Å^3, Z = 2, μ(CuKα) = 24.89 cm^{-1}, d_{calc} = = 1.811 g cm^{-3}. 4423 reflections measured, 4180 unique (R_{int} = 0.0634), 3739 observed with $F_0 > 4\sigma(F_0)$, 326 parameters. The final $R_1(F^2)$ was 0.0739 ($> 2\sigma I$) and wR_2 (all data) = 0.2172. Goodness-of-fit on F^2 was 1.043, largest difference peak and hole are 0.449 and –0.476 eÅ^3.

Crystallographic data for **6**: $C_{19}H_8ClF_{12}O_4P$, M = 594.67, colourless prism of dimensions 0.3×0.2×0.15 mm^3, triclinic, space group $P\bar{1}$, at 123 K, a = 9.935(3), b = 10.567(2) and c = 11.305(2) Å, α = 98.15(2)°, β = 108.01(2)°, γ = 107.36(3)°, V = 1040.9(5) Å^3, Z = 2, μ(CuKα) = = 36.56 cm^{-1}, d_{calc} = 1.897 g cm^{-3}. 4402 reflections measured, 4167 unique (R_{int} = 0.1516), 3749 observed with $F_0 > 4\sigma(F_0)$, 336 parameters. The final $R_1(F^2)$ was 0.1215 ($> 2\sigma I$) and wR_2 (all data) = 0.3125. Goodness-of-fit on F^2 was 1.510, largest difference peak and hole are 0.326 and –0.406 eÅ^3.

CCDC 689215 and 689216 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, 2009.

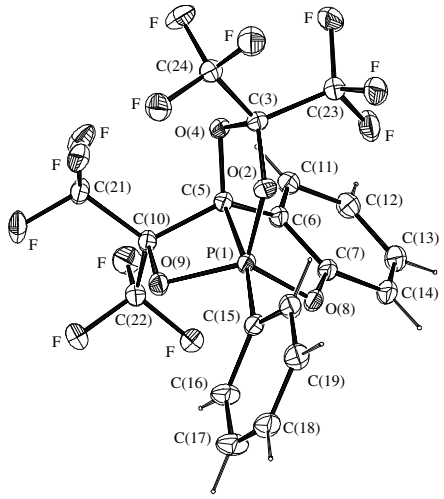


Figure 2 Molecular geometry of compound **5** in a crystal. Selected bond lengths (Å): P(1)–O(8) 1.623(2), P(1)–O(2) 1.649(3), P(1)–O(9) 1.670(2), P(1)–C(15) 1.804(3), P(1)–C(5) 1.879(3), O(9)–C(10) 1.435(4), C(10)–C(5) 1.561(4); selected bond angles (°): O(8)–P(1)–O(2) 116.9(1), O(8)–P(1)–O(9) 122.6(1), O(2)–P(1)–O(9) 119.0(1), O(8)–P(1)–C(15) 93.7(1), O(2)–P(1)–C(15) 94.8(1), O(9)–P(1)–C(15) 94.2(1), O(8)–P(1)–C(5) 91.7(1), O(2)–P(1)–C(5) 88.3(1), O(9)–P(1)–C(5) 77.6(1), C(15)–P(1)–C(5) 171.7(1), C(10)–O(9)–P(1) 99.2(2), O(9)–C(10)–C(5) 96.1(2), C(10)–C(5)–P(1) 86.6(2).

the contrary, another apical bond (P^1–C^5) is rather long. The oxaphosphetane cycle $P^1O^9C^{10}C^5$ is planar within 0.046(7) Å (**5**), 0.023(9) Å (**6**) [atoms O^2, O^4, O^8, C^6, C^{21}, C^{22} are deviated from this plane by –1.360(2), –1.303(2), 1.428(2), 1.136(3), –1.114(4), 1.368(3) Å (**5**) and 1.326(3), 1.280(3), –1.441(3), –1.180(4), –1.365(4), 1.165(5) Å (**6**), respectively], as well as the five-membered cycle $P^1C^5C^6C^7O^8$, which is planar within 0.028(7) Å (**5**) [atoms O^2, O^9, O^4, C^{10}, C^{11} are deviated from this plane by –1.513(2), 1.325(2), –1.063(2), 1.364(3), 0.063(3) Å] and 0.027(4) Å (**6**) [atoms O^2, O^9, O^4, C^{10} are deviated from this plane by 1.564(3), –1.358(3), 1.062(3), –1.362(4), 0.057(4) Å]. Dihedral angle between plane $P^1C^5C^6C^7O^8$ and phenyl group is 81.7(2)° (**5**) and 23.7(2)° (**6**). Dioxaphospholane cycle ($P^1O^2C^3O^4C^5$) has an 'envelope' conformation [the fragment $C^3O^2P^1C^5$ is planar within 0.000(7) (**5**) and 0.016(9) Å (**6**), atom O^4 deviates from the plane by –0.261(2) (**5**) and 0.291(3) Å (**6**)].

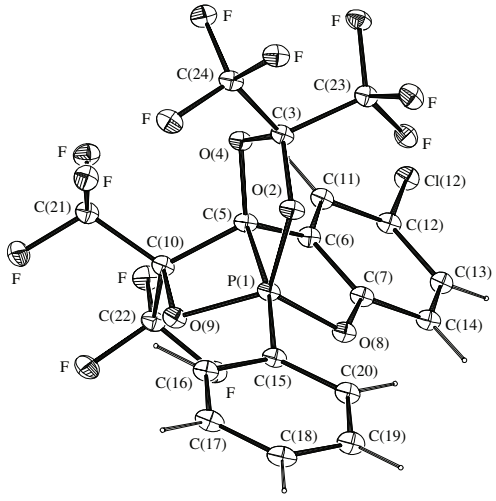
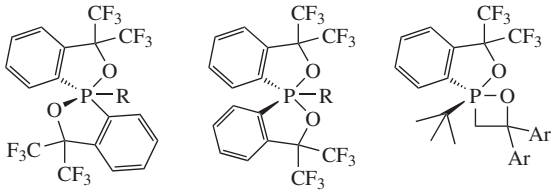


Figure 3 Molecular geometry of compound **6** in a crystal. Selected bond lengths (Å): C(5)–O(4) 1.436(4), C(5)–C(10) 1.546(5), C(5)–P(1) 1.881(4), C(10)–O(9) 1.440(4), C(15)–P(1) 1.808(3), O(2)–P(1) 1.669(3), O(8)–P(1) 1.623(3), O(9)–P(1) 1.663(3); selected bond angles (°): C(10)–C(5)–P(1) 86.9(2), O(9)–C(10)–C(5) 96.1(3), C(10)–O(9)–P(1) 99.3(2), O(8)–P(1)–O(9) 119.4(2), O(8)–P(1)–O(2) 115.0(2), O(9)–P(1)–O(2) 123.8(2), O(8)–P(1)–C(15) 95.7(2), O(9)–P(1)–C(15) 94.8(2), O(2)–P(1)–C(15) 93.0(1), O(8)–P(1)–C(5) 91.6(2), O(9)–P(1)–C(5) 77.4(2), O(2)–P(1)–C(5) 88.2(1), C(15)–P(1)–C(5) 171.3(2).



7 **8** **9**

The reactions of 4,4-bis(trifluoromethyl)-4,5-dihydro-2-phenylbenzo[*e*]- and 4,4-bis(trifluoromethyl)-4,5-dihydro-2-phenyl-(4′-chlorobenzo)[*e*]-1,3,2-dioxaphosphepin-5-ones **3**, **4** with hexafluoroacetone, in spite of the relative rigidity of the molecules, lead to the formation of unusual propeller-like structures, namely, 5-carbaphosphatranes **5**, **6**, containing three small cycles annelated along a P–C bond. These compounds are formed in the result of the simultaneous participation in the reaction of two active centres such as phosphorus atom and endocyclic carbonyl group.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.01.014.

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