Syntheses and Spectroscopic Studies of Some New Diazaphospholes and Diazaphosphorinanes. Crystal Structure of 4-F-$C_6H_4C(O)N(H)P(O)(NHC_6H_4NH)$

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New diazaphospholes and diazaphosphorinanes with formula 4-F-$C_6H_4C(O)NHP(O)(NHC_6H_4NH)$ (**1**), 4-CH_3-$C_6H_4NHP(O)(NHC_6H_4NH)$ (**2**), 4-CH_3-$C_6H_4NHP(O)(NHC_{10}H_6NH)$ (**3**), 4-CH_3-$C_6H_4NHP(O)(NHCH_2C_6H_4NH)$ (**4**), 4-F-$C_6H_4C(O)NHP(O)(NHCH_2C_6H_4NH)$ (**5**), $CCl_3C(O)NHP(O)(NHCH_2C_6H_4NH)$ (**6**) and 4-CH_3-$C_6H_4NHP(O)(NHCH_2C(CH_3)_2CH_2NH)$ (**7**) were synthesized and characterized by ^{1}H, ^{13}C, ^{31}P NMR and IR spectroscopy and elemental analysis. The structure of compound **1** has been determined by X-ray crystallography. A one-dimensional polymeric chain was observed in the crystalline lattice produced by intermolecular -P=O…H-N- and -C=O…H-N-hydrogen bonds. Compounds **1** and **2** contain five-membered rings and show high values for ^2J(PNH) and ^2J(P,C) coupling constants due to the ring strain. These constants are reduced seriously in compounds with six-membered rings. In compound **6** with $CCl_3C(O)NH$ moiety, all phosphorus-hydrogen couplings are zero.

Key words: X-Ray Crystallography, NMR Spectroscopy, Diazaphosphorinane, Diazaphosphole

Introduction

Near range phosphorus-carbon and phosphorus-hydrogen coupling constants are important due to their application in spectral assignments and in the study of chemical bonds [1, 2]. Several publications have reported information *e. g.* on the bridge effect in geminal P-C coupling constants [3], the orientation of lone pairs [4] and the stereochemical dependence [5]. In previous work, we studied $^{2,3}J$(P,X) coupling constants (X = H, C) in phosphoric triamides and phosphoramidic acid esters [6 – 9]. Furthermore, we considered the hybridization effect on these couplings and relations of the strength of P-N bonds (obtained by single crystal X-ray determination) in some diazaphospholes and diazaphosphorinanes [10]. To extend this matter, we synthesized some benzodiazaphospholes, and diaza-, and benzodiazaphosphorinanes. Also, we determined the structure of the benzodiazaphosphole 4-F-$C_6H_4C(O)NHP(O)(NHC_6H_4NH)$ for comparison with other phosphoramidates [11] in order to obtain an explanation for the high value ^2J(P,X).

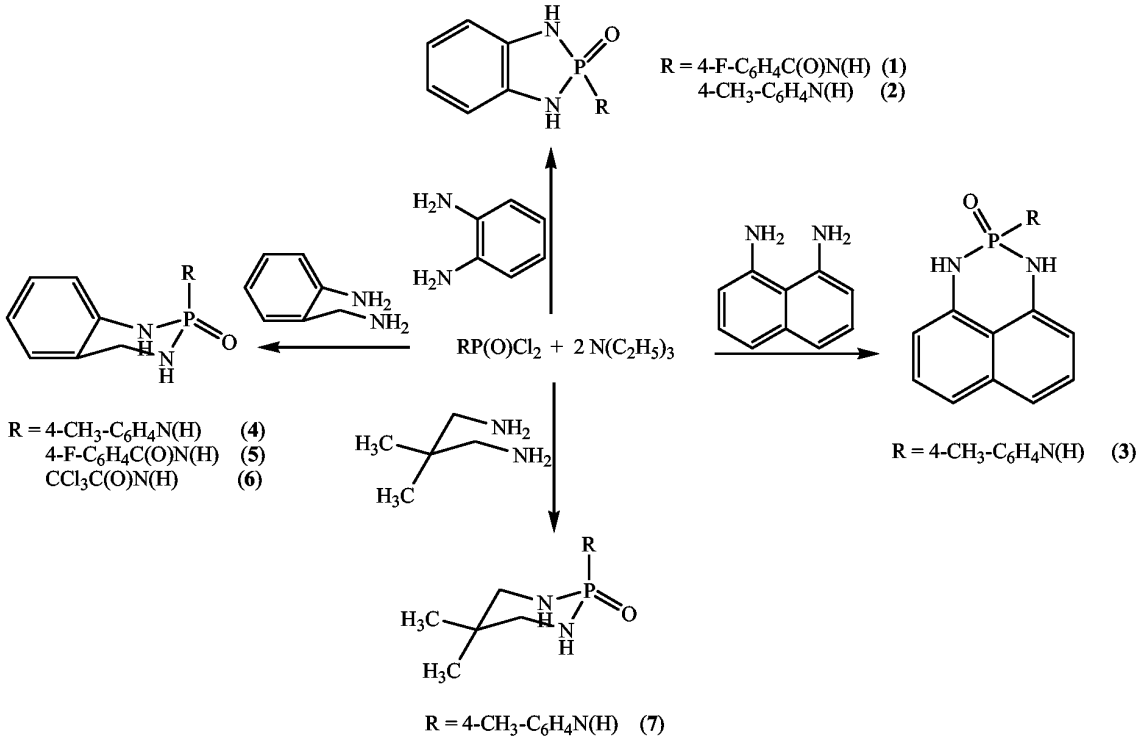
Results and Discussion

NMR study

Scheme 1 indicates the synthesis pathway to the new benzodiazaphospholes, and diaza-, and benzodiazaphosphorinanes **1** – **7**. Phosphorus-hydrogen and phosphorus-carbon coupling constants (Hz) and $\delta(^{31}\mathrm{P})$ (ppm) data of these compounds are listed in Table 1. The ^{1}H NMR spectrum of compound **1** (as well as of **2**) shows a doublet signal for the two equivalent amino protons (of the five-membered ring) with a high value for the two bonds phosphorus-hydrogen coupling constant ($^2J(\mathrm{PNH}) = 17.9$ Hz for **1** and 17.2 Hz for **2**). Such high value coupling constants were not observed for acyclic phosphoramidates [6 – 10, 12 – 13]. $^2J(\mathrm{PNH})$ coupling constants of endocyclic amino protons in compounds **3**, **4** and **7** (containing six-membered rings and identical exocyclic group) are 4.5, 7.8 and 4.3 Hz, respectively. The major reduction of the $^2J(\mathrm{PNH})$ coupling constant from 17.9 Hz (in **1**) to 4.3 Hz (in **7**) is due to the increase of ring size. The ^{1}H NMR spectra of compounds **4** and **5** show two sep-

Compound	$^2J(\mathrm{PNH})_{\mathrm{exocyclic}}$	$^2J(\mathrm{PNH})_{\mathrm{endocyclic}}$	$^2J(\mathrm{P,C})$	$^3J(\mathrm{P,C})$	$\delta(^{31}\mathrm{P})$
1	8.1	17.9	14.3	13.3 (ring) 8.8 (*p*-fluorobenzamide)	13.10
2	8.6	17.2	13.5	12.4 (ring) 7.7 (*p*-toluidine)	12.15
3	8.9	4.5	0	10.2 (ring) 7.7 (*p*-toluidine)	−10.39
4	4.6	7.8 (aromatic) 0 (aliphatic)	2.8 (CH_2), 7.0 (ring)	9.2 (ring) 6.9 (*p*-toluidine)	2.54
5	8.3	5.8 (aromatic) 0 (aliphatic)	0 (CH_2), 7.2 (ring)	9.6 (ring) 8.7 (*p*-fluorobenzamide)	0.09
6	0	0	0	6.5 (CCl_3)	−18.15
7	0	4.3	6.5	6.8	5.19

Table 1. $^{2,3}J(\mathrm{P,X})$ (X = H, C) coupling constants (Hz) and $\delta(^{31}\mathrm{P})$ (ppm) of compounds **1**–**7**.



Scheme 1. The preparation of compounds **1**–**7**.

arate signals for the two unequivalent endocyclic NH protons with $^2J(\mathrm{PNH_{aromatic}}) > {}^2J(\mathrm{PNH_{aliphatic}})$, similar to our previous result for compound $C_6H_5C(O)NHP(O)(NHCH_2C_6H_4NH)$ [10]. The exocyclic amino protons in molecules **1**–**5** give rise to doublet signals produced by $^2J(\mathrm{PNH})$ coupling. In compound **6** with its $CCl_3C(O)NH$ moiety, no phosphorus-hydrogen couplings are discernible (Table 1).

Similar to $^2J(\mathrm{PNH})$ coupling constant, high values of $^2J(\mathrm{P,C})_{\mathrm{aromatic}}$ were observed for the benzodiazaphospholes **1** and **2** (14.3 and 13.5 Hz, respectively) which are larger than the values of acyclic phosphoramidates [6–9]. The exocyclic group in these compounds also shows non-zero $^3J(\mathrm{P,C})$ coupling constants (Table 1). In molecule **6**, only the coupling of the CCl_3 carbon atom with the phosphorus atom was observed ($^3J(\mathrm{P,C}) = 6.5$ Hz). $^2J(\mathrm{P,C})$ for aliphatic carbon atoms in **7** is 6.5 Hz, which is reduced to 2.8 Hz in **4** and to zero in compounds **5** and **6**.

The phosphorus chemical shifts, $\delta(^{31}\mathrm{P})$, of compounds **1**–**7** appear in the range from −18.15 ppm (in **6**) to 13.10 ppm (in **1**). ^{31}P nuclei in compounds **1** and **2** are deshielded relative to those of other compounds.

Table 2. Crystallographic data for compound **1**.

Empirical formula	$C_{13}H_{11}FN_3O_2P$
Formula weight	291.22
Temperature [K]	120(2)
Wavelength [Å]	0.71073
Crystal system, space group	monoclinic, $C2/c$
Unit cell dimensions	$a = 20.764(6)$ Å
	$\alpha = 90.0^\circ$
	$b = 4.9008(14)$ Å
	$\beta = 104.725(7)^\circ$
	$c = 25.868(7)$ Å
	$\gamma = 90.0^\circ$
V [Å^3]	2545.8(12)
Z, Calculated density	8, 1.520 gcm^{-3}
Absorption coefficient [mm^{-1}]	0.233
$F(000)$	1200
Crystal size [mm^3]	$0.15 \times 0.20 \times 0.25$
θ Range for data collection [°]	2.03 to 28.07
Limiting indices	$-27 \le h \le 27$
	$-6 \le k \le 6$
	$-30 \le l \le 34$
Reflections collected / unique	9801 / 3069 [R(int)=0.1158]
Completeness to theta = 28.07°	98.8%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3069 / 0 / 181
Goodness-of-fit on F^2	0.997
Final R indices	$R_1 = 0.0686$, $wR_2 = 0.1344$
R Indices (all data)	$R_1 = 0.1319$, $wR_2 = 0.1510$
Max. and min. transmission	0.928 and 0.355
Largest diff. peak and hole	0.568 and -0.657 e.Å^{-3}

Table 3. Selected bond lengths (Å) and angles (°) for compound **1**.

P(1)-O(1)	1.476(2)	N(1)-C(1)	1.396(4)
P(1)-N(1)	1.640(3)	N(2)-C(2)	1.412(4)
P(1)-N(2)	1.652(3)	N(3)-C(7)	1.369(4)
P(1)-N(3)	1.671(3)	F(1)-C(11)	1.362(4)
O(2)-C(7)	1.233(4)	C(1)-C(6)	1.382(4)
N(1)-P(1)-N(2)	93.63(14)	N(2)-P(1)-N(3)	108.95(15)
O(1)-P(1)-N(1)	116.16(15)	C(1)-N(1)-P(1)	112.9(2)
O(1)-P(1)-N(2)	119.53(14)	C(2)-N(2)-P(1)	111.4(2)
O(1)-P(1)-N(3)	105.68(14)	C(7)-N(3)-P(1)	123.3(2)
N(1)-P(1)-N(3)	112.72(14)	F(1)-C(11)-C(12)	118.8(3)

X-ray crystallography

Single crystals of compound **1** were obtained from a solution in methanol and chloroform after slow evaporation at room temperature. The crystal data and the details of the X-ray analysis are given in Table 2 and selected bond lengths and angles in Table 3. The molecular structure and the unit cell packing are shown in Figs 1 and 2.

The nitrogen environments in the structure of benzodiazaphosphole **1** are nearly planar. The sum of the surrounding angles at N(1) and N(2) are only

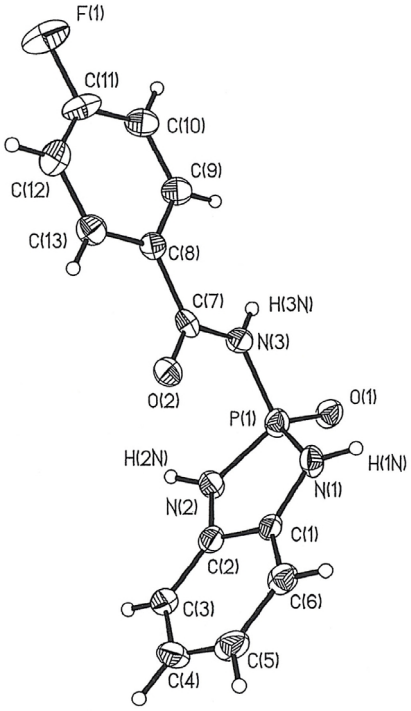


Fig. 1. Molecular structure and atom-labeling scheme for 4-F-$C_6H_4C(O)NHP(O)(NHC_6H_4NH)$ (50% probability ellipsoids).

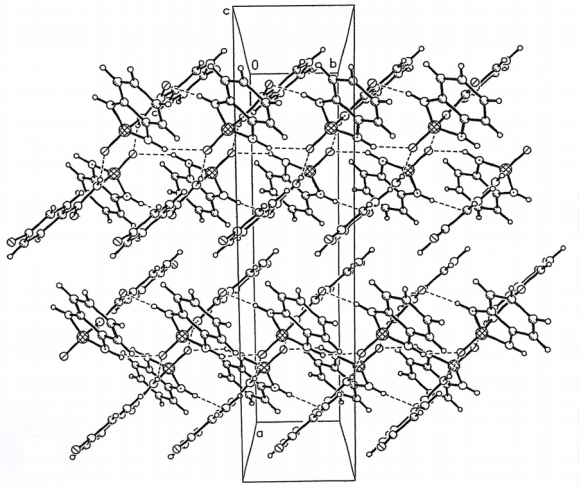


Fig. 2. A view of the unit cell for compound 4-F-$C_6H_4C(O)NHP(O)(NHC_6H_4NH)$.

slightly lower than sp^2 angles, 358.63° and 355.62°, respectively. The internal angles P(1)-N(1)-C(1) and P(1)-N(2)-C(2) are 112.9(2)° and 111.4(2)°. Similarly, in two polymorphs of diazaphosphole ox-

Table 4. Hydrogen bonds D-H···A for compound **1** (Å and °).

D-H···A	*d*(D-H)	*d*(H··A)	∠DHA	*d*(D··A)
N1-H1N··O2 $[x,y+1,z]$	0.838	2.118	153.68	2.893(3)
N2-H2N··O1 $[x,y-1,z]$	0.914	2.288	149.37	3.110(3)
N3-H3N··O1 $[-x+1/2,-y+1/2,z]$	0.813	2.143	162.05	2.927(3)

ide $C_6H_5\overline{P(O)[NHC_6H_4NH]}$ [14], the internal P-N-C angles are 112.2(1)° and 112.5(3)°. The endocyclic P(1)-N(1) and P(1)-N(2) bonds (1.640(3) and 1.652(3) Å) are shorter than the exocyclic P(1)-N(3) bond (1.671(3) Å) and the P-N bonds in acyclic phosphoramidates [15–18]. All P-N bond lengths of **1** are smaller than a standard P-N single bond (1.77 Å) [19]. It seems that the strong P-N bonds in five-membered rings lead to high value $^2J(\mathrm{PNH})$ coupling constants. Such strong P-N bonds were also observed in diazaphosphole 4-CH_3-$C_6H_4O\overline{P(O)(NHCH_2CH_2N}C_6H_5)$ [10]. The phosphorus atom in compound **1** has a distorted tetrahedral configuration with the angles in the range from 119.53(14)° (O(1)-P(1)-N(2)) to 93.63(14)° (internal angle N(1)-P(1)-N(2)). The P=O bond lengths in this molecule (1.476(2) Å) is slightly longer than the standard PO double bond length (1.45 Å) [19]. We previously reported the structure of diazaphosphorinane **7** [11] where the P(1)-O(1) bond length is slightly smaller (1.4852(10) Å).

Compound **1** forms one-dimensional polymeric chains *via* intermolecular -P=O…H-N- and -C=O…H-N- hydrogen bonds (Table 4). The centrosymmetric dimer which is produced by two equal P(1)-O(1)…H(3N)-N(3) hydrogen bonds are connected into chains *via* the intermolecular C(7)-O(2)…H(1N)-N(1) and P(1)-O(1)…H(2N)-N(2) hydrogen bonds.

Experimental Section

X-ray measurements

X-ray data of compound **1** was collected on a Bruker SMART 1000 CCD single crystal diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The structure was refined with SHELXL-97 [20] by full matrix least squares on F^2. The positions of hydrogen atoms were obtained from the difference Fourier map. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program [21]. Crystallographic data for this structure have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC 259193 ($C_{13}H_{11}F_1N_3O_2P_1$). Copies of the data can be obtained, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Spectroscopic measurements

All reactions were performed under argon atmosphere and in dry solvents. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^{1}H and ^{13}C chemical shifts were determined relative to internal TMS, ^{31}P chemical shifts relative to 85% H_3PO_4 as external standard. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. 4-CH_3-$C_6H_4NHP(O)Cl_2$ [22], 4-F-$C_6H_4C(O)NHP(O)Cl_2$ [23] and $CCl_3C(O)NHP(O)Cl_2$ [24] were prepared according to the literature method.

Syntheses

2-(N-p-Fluorobenzoyl)-2-oxo-1,3,2-benzodiazaphosphole ***(1)***

A mixture of 1,2-phenylenediamine (0.195 g, 1.8 mmol) and triethylamine (0.364 g, 3.6 mmol) in chloroform (20 ml) was added at −5 °C to a solution of *N*-(4-fluorobenzoyl) phosphoramidic dichloride (0.461 g, 1.8 mmol) in chloroform (10 ml) and stirred for 6 h. The product was filtered and washed with chloroform (yield: 0.30 g, 57%).

M. p. 289 °C. – IR (film): $\tilde{\nu} = 3290$ (NH), 1660 (C=O), 1430, 1392, 1286, 1186 (P=O), 911 (P-N), 736 (P-N) cm^{-1}. – ^{1}H NMR (500.13 MHz, d_6-DMSO): $\delta = 6.64$ (s, 4 H, Ar-H), 7.26 (t, ^3J[(H,H),(F,H)] = 8.5 Hz, 2 H, Ar-H), 8.01 (dd, ^3J(H,H) = 7.8 Hz, ^4J(F,H) = 5.6 Hz, 2 H, Ar-H), 8.57 (d, ^2J(PNH) = 17.9 Hz, 2 H, NH), 9.98 (d, ^2J(PNH) = 8.1 Hz, 1 H, NH). – ^{13}C NMR (125.77 MHz, d_6-DMSO): δ = 109.34 (d, ^3J(P,C) = 13.3 Hz), 115.23 (d, ^2J(F,C) = 22.0 Hz), 118.77 (s), 129.70 (dd, ^4J(F,C) = 2.8 Hz, ^3J(P,C) = 8.8 Hz, 1 C, CH), 130.94 (d, ^3J(F,C) = 9.3 Hz), 132.79 (d, ^2J(P,C) = 14.3 Hz), 163.48 (d, ^1J(F,C) = 250.5 Hz, 1 C, CH), 168.82 (s, 1 C, C=O). – ^{31}P NMR (202.46 MHz, d_6-DMSO): $\delta = 13.10$ (m). – $C_{13}H_{11}FN_3O_2P$ (291.2): calcd. C 53.62, H 3.81, N 14.43; found C 53.60, H 3.81, N 14.44.

2-(p-Methylanilino)-2-oxo-1,3,2-benzodiazaphosphole ***(2)***

A mixture of 1,2-phenylenediamine (0.140 g, 1.3 mmol) and triethylamine (0.263 g, 2.6 mmol) in acetonitrile (15 ml) was added at −5 °C to a solution of *N*-(4-methylphenyl) phosphoramidic dichloride (0.291 g, 1.3 mmol) in acetonitrile (10 ml) and stirred for 5 h. The product was filtered and washed with acetonitrile and chloroform (yield: 0.17 g, 51%).

M. p. 265 °C. – IR (film): $\tilde{\nu} = 3335$ (NH), 3150 (NH), 1500, 1398, 1300, 1180 (P=O), 985 (P-N), 733 (P-N),

688 cm^{-1}. – ^1H NMR (500.13 MHz, d_6-DMSO): $\delta = 2.10$ (s, 3 H, *p*-CH_3), 6.43 (d, $^3J(H,H) = 8.0$ Hz, 2 H, Ar-H), 6.69 (s, 4 H, Ar-H), 6.82 (d, $^3J(H,H) = 8.0$ Hz, 2 H, Ar-H), 7.79 (d, $^2J(PNH) = 8.6$ Hz, 1 H, NH), 8.41 (d, $^2J(PNH) = 17.2$ Hz, 2 H, NH). – ^{13}C NMR (125.77 MHz, d_6-DMSO): $\delta = 20.55$ (s, *p*-CH_3), 109.90 (d, $^3J(P,C) = 12.4$ Hz), 117.51 (d, $^3J(P,C) = 7.7$ Hz), 119.43 (s), 129.20 (s), 129.59 (s), 132.44 (d, $^2J(P,C) = 13.5$ Hz), 140.09 (s). – ^{31}P NMR (202.46 MHz, d_6-DMSO): $\delta = 12.15$ (m). – $C_{13}H_{14}N_3OP$ (259.2): calcd. C 60.23, H 5.44, N 16.21; found C 60.21, H 5.43, N 16.20.

*2-(p-Methylanilino)-2-oxo-1,3,2-naphtodiazaphosphorinane (**3**)*

To a solution of *N*-(4-methylphenyl) phosphoramidic dichloride (0.314 g, 1.4 mmol) in acetonoitrile (10 ml), a mixture of 1,8-naphtalenediamine (0.221 g, 1.4 mmol) and triethylamine (0.283 g, 2.8 mmol) in acetonitrile (15 ml) was added at −5 °C and stirred for 6 h. The product was filtered and washed with chloroform (yield: 0.27 g, 63%).

M. p. 248 °C. – IR (film): $\tilde{\nu} = 3165$ (NH), 2916, 1588, 1379, 1176 (P=O), 1064, 806 (P-N), 751 (P-N) cm^{-1}. – ^1H NMR (500.13 MHz, d_6-DMSO): $\delta = 2.11$ (s, 3 H, *p*-CH_3), 6.55 (d, $^3J(H,H) = 7.3$ Hz, 2 H, Ar-H), 6.87 (s, 4 H, Ar-H), 7.11 (d, $^3J(H,H) = 8.2$ Hz, 2 H, Ar-H), 7.16 (t, $^3J(H,H) = 7.7$ Hz, 2 H, Ar-H), 7.77 (d, $^2J(PNH) = 8.9$ Hz, 1 H, NH), 8.57 (d, $^2J(PNH) = 4.5$ Hz, 2 H, NH). – ^{13}C NMR (125.77 MHz, d_6-DMSO): $\delta = 20.59$ (s, *p*-CH_3), 108.01 (d, $^3J(P,C) = 10.2$ Hz), 117.71 (d, $^3J(P,C) = 7.7$ Hz), 118.32 (s), 127.81 (s), 129.16 (s), 129.59 (s), 135.64 (s), 139.96 (s), 140.30 (s). – ^{31}P NMR (202.46 MHz, d_6-DMSO): $\delta = -10.39$ (m). – $C_{17}H_{16}N_3OP$ (309.3): calcd. C 66.01, H 5.21, N 13.59; found C 65.97, H 5.20, N 13.57.

*2-(p-Methylanilino)-2-oxo-1,3,2-benzodiazaphosphorinane (**4**)*

To a solution of *N*-(4-methylphenyl) phosphoramidic dichloride (0.314 g, 1.4 mmol) in acetonitrile (10 ml), a mixture of 2-aminobenzylamine (0.171 g, 1.4 mmol) and triethylamine (0.283 g, 2.8 mmol) in acetonitrile (15 ml) was added at −5 °C and stirred for 6 h. The product was filtered and washed with chloroform (yield: 0.20 g, 52%).

M. p. 185 °C. – IR (film): $\tilde{\nu} = 3162$ (NH), 2919, 1611, 1516, 1475, 1201, 1169 (P=O), 968 (P-N), 812 (P-N), 746 cm^{-1}. – ^1H NMR (500.13 MHz, d_6-DMSO): $\delta = 2.16$ (s, 3 H, *p*-CH_3), 3.87 (m, 1 H, CH), 4.01 (m, 1 H, CH), 4.95 (s, 1 H, NH), 6.72 (d, $^3J(H,H) = 8.0$ Hz, 2 H, Ar-H), 6.89 (d, $^3J(H,H) = 7.2$ Hz, 2 H, Ar-H), 6.96 (m, 3 H, Ar-H), 7.03 (t, $^3J(H,H) = 7.4$ Hz, 1 H, Ar-H), 7.46 (d, $^2J(PNH) = 7.8$ Hz, 1 H, NH), 7.97 (d, $^2J(PNH) = 4.6$ Hz, 1 H, NH). – ^{13}C NMR (125.77 MHz, d_6-DMSO): $\delta = 20.67$ (s, *p*-CH_3), 43.38 (d, $^2J(P,C) = 2.8$ Hz, CH_2), 116.91 (d, $^3J(P,C) = 9.2$ Hz), 118.03 (d, $^3J(P,C) = 6.9$ Hz), 119.76 (s), 124.36 (d, $^2J(P,C) = 7.0$ Hz), 126.43 (s), 127.84 (s), 128.70 (s), 129.39 (s), 140.17 (s), 142.33 (s). – ^{31}P NMR (202.46 MHz, d_6-DMSO): $\delta = 2.54$ (m). – $C_{14}H_{16}N_3OP$ (273.3): calcd. C 61.53, H 5.90, N 15.38; found C 61.50, H 5.89, N 15.39.

*2-(N-p-Fluorobenzoyl)-2-oxo-1,3,2-benzodiazaphosphorinane (**5**)*

A mixture of 2-aminobenzylamine (0.195 g, 1.6 mmol) and triethylamine (0.323 g, 3.2 mmol) in chloroform (20 ml) was added at −5 °C to a solution of *N*-(4-fluorobenzoyl) phosphoramidic dichloride (0.410 g, 1.6 mmol) in chloroform (10 ml) and stirred for 7 h. The product was filtered and washed with chloroform (yield: 0.24 g, 49%).

M. p. 225 °C. – IR (film): $\tilde{\nu} = 3287$ (NH), 3185 (NH), 1666, 1604, 1471, 1449, 1401, 1181 (P=O), 1164, 1091, 946 (P-N), 903, 753 (P-N) cm^{-1}. – ^1H NMR (500.13 MHz, d_6-DMSO): $\delta = 3.90$ (dd, $^2J(H,H) = 14.9$ Hz, $^3J(P,H) = 25.3$ Hz, 1 H, CH), 4.43 (dd, $^2J(H,H) = 14.9$ Hz, $^3J(P,H) = 8.9$ Hz, 1 H, CH), 5.40 (b, 1 H, NH), 6.76 (d, $^3J[(F,H),(H,H)] = 7.8$ Hz, 2 H, Ar-H), 6.99 (d, $^3J(H,H) = 7.3$ Hz, 1 H, Ar-H), 7.04 (t, $^3J(H,H) = 6.6$ Hz, 1 H, Ar-H), 7.26 (t, $^3J(H,H) = 8.8$ Hz, 2 H, Ar-H), 7.97 (d, $^2J(PNH) = 5.8$ Hz, 1 H, NH), 8.03 (dd, $^3J(H,H) = 8.3$ Hz, $^4J(F,H) = 5.6$ Hz, 2 H, Ar-H), 9.65 (d, $^2J(PNH) = 8.3$ Hz, 1 H, NH). – ^{13}C NMR (125.77 MHz, d_6-DMSO): $\delta = 43.19$ (s, CH_2), 115.11 (d, $^2J(F,C) = 21.6$ Hz), 116.84 (d, $^3J(P,C) = 9.6$ Hz), 119.71 (s), 124.22 (d, $^2J(P,C) = 7.2$ Hz), 125.78 (s), 127.10 (s), 130.20 (dd, $^4J(F,C) = 2.9$ Hz, $^3J(P,C) = 8.7$ Hz, 1 C, CH), 130.89 (d, $^3J(F,C) = 9.2$ Hz), 140.22 (s), 163.37 (d, $^1J(F,C) = 249.5$ Hz, 1 C, CH), 167.12 (s, 1 C, C=O). – ^{31}P NMR (202.46 MHz, d_6-DMSO): $\delta = 0.09$ (m). – $C_{14}H_{13}FN_3O_2P$ (305.2): calcd. C 55.09, H 4.29, N 13.77; found C 55.07, H 4.29, N 13.76.

*2-(N-Trichloroacethyl)-2-oxo-1,3,2-benzodiazaphosphorinane (**6**)*

A mixture of 2-aminobenzylamine (0.207 g, 1.7 mmol) and triethylamine (0.343 g, 3.4 mmol) in acetonitrile (20 ml) was added at −5 °C to a solution of *N*-trichloroacetyl phosphoramidic dichloride (0.475 g, 1.7 mmol) in acetonitrile (15 ml) and stirred for 5 h. The product was filtered and washed with acetonitrile and chloroform (yield: 0.31 g, 56%).

M. p. 239 °C. – IR (film): $\tilde{\nu} = 2903$, 2655, 1713 (C=O), 1456, 1255, 1223 (P=O), 1124, 981, 954 (P-N), 884 (P-N), 824, 683, 488 cm^{-1}. – ^1H NMR (500.13 MHz, d_6-DMSO): $\delta = 3.98$ (s, 2 H, CH_2), 5.35 (b, 1 H, NH), 6.76 (t, $^3J(H,H) = 7.4$ Hz, 1 H, Ar-H), 6.87 (d, $^3J(H,H) = 7.7$ Hz, 1 H, Ar-H), 7.13 (t, $^3J(H,H) = 7.4$ Hz, 1 H, Ar-H), 7.22 (d, $^3J(H,H) = 7.7$ Hz, 1 H, Ar-H), 8.11 (b, 1 H, NH), 9.80 (b, 1 H, NH). – ^{13}C NMR (125.77 MHz, d_6-DMSO): $\delta = 38.42$ (s, CH_2), 93.15 (d, $^3J(P,C) = 6.5$ Hz, CCl_3),

117.61 (s), 119.14 (s), 119.71 (s), 129.55 (s), 130.58 (s), 143.12 (s), 160.95 (s, 1 C, C=O). – ^{31}P NMR (202.46 MHz, d_6-DMSO): $\delta = -18.15$ (s). – $C_9H_9Cl_3N_3O_2P$ (328.5): calcd. C 32.90, H 2.76, N 12.79; found C 32.88, H 2.76, N 12.80.

*5,5-Dimethyl-2-(p-methylanilino)-2-oxo-1,3,2-diazaphosphorinane (**7**)*

A solution of 2,2-dimethylpropylenediamine (0.173 g, 1.7 mmol) and triethylamine (0.343 g, 3.4 mmol) in chloroform (25 ml) was added dropwise to a stirred solution of *N*-(4-methylphenyl) phosphoramidic dichloride (0.381 g, 1.7 mmol) in chloroform (10 ml) at -5 °C. After 8 h the precipitate was filtered, washed with distilled water (25 ml) and recrystallized from a methanol/heptane mixture (yield: 0.29 g, 68%).

M. p. 216 °C. – IR (film): $\tilde{\nu} = 3299$ (NH), 3218 (NH), 3189, 2958, 1619, 1517, 1309, 1186 (P=O), 1177, 1095, 964, 943 (P-N), 814 (P-N), 573 cm^{-1}. – ^{1}H NMR (500.13 MHz, d_6-DMSO): $\delta = 0.68$ (s, 3 H, CH_3), 1.01 (s, 3 H, CH_3), 2.16 (s, 3 H, *p*-CH_3), 2.51 (ddd, ^2J(H,H) = 12.2 Hz, ^3J(H,H) = 5.0 Hz, ^3J(P,H) = 24.8 Hz, 2 H, 2 CH), 2.78 (dd, ^2J(H,H) = 12.2 Hz, ^3J(H,H) = 5.0 Hz, 2 H, 2 CH), 4.32 (d, ^2J(PNH) = 4.3 Hz, 2 H, NH), 6.89 (b, 1 H, NH), 6.91 (d, ^3J(H,H) = 7.5 Hz, 2 H, Ar-H), 6.96 (d, ^3J(H,H) = 7.5 Hz, 2 H, Ar-H). – ^{13}C NMR (125.77 MHz, d_6-DMSO): $\delta = 20.69$ (s), 23.09 (s), 25.29 (s), 30.47 (d, ^2J(P,C) = 6.5 Hz), 53.80 (s), 117.93 (d, ^3J(P,C) = 6.8 Hz), 128.27 (s), 129.27 (s), 140.90 (s). – ^{31}P NMR (202.46 MHz, d_6-DMSO): $\delta = 5.19$ (m). – $C_{12}H_{20}N_3OP$ (253.3): calcd. C 56.90, H 7.96, N 16.59; found C 56.84, H 7.95, N 16.57.

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