1,8-Bis(phosphanyl)naphthalenes: 1,8-Bis[(diethylamino)phosphanyl]naphthalene, 1,8-Bis(dichlorophosphanyl)naphthalene, and 1,3-Dichloro-2,3-dihydro-1,3-dioxo-2-oxa-1,3-diphosphaphenalene☆

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1,8-Dilithionaphthalene **1** reacted with bis(diethylamino)chlorophosphane to form 1,8-bis[(diethylamino)phosphanyl]naphthalene **2**, whose structure was confirmed by X-ray crystal structure analysis; there are two independent molecules, in which the $P(NEt_2)_2$ groups adopt an eclipsed conformation. Reaction of **2** with gaseous HCl gave in low yield 1,8-bis(dichlorophosphanyl)naphthalene **3**, which was characterized by ^1H- and ^{31}P-NMR spectroscopy, mass spectrometry and elemental analysis. Attempted recrystallization of **3** led to oxidative hydrolysis which furnished **4**, an anhydride of a bis(chlorophosphonic acid), whose structure was elucidated by X-ray crystal structure analysis. The geometry of **4** reveals a relief of strain from the bis(aminophosphane) **2**; the naphthalene groups are less distorted and the P atoms are displaced less far from the naphthalene best plane.

Steric strain associated with 1,8-disubstituted naphthalenes (*peri*-substitution) has received much attention[1]. Relief of such strain may be accomplished by in-plane or out-of-plane displacement of the substituents, and distortion or buckling of the aromatic nucleus itself. A number of 1,8-bis(dialkylphosphanyl)naphthalenes, a 1,8-bis(alkylarylphosphanyl)naphthalene, and a 1,8-bis(diarylphosphanyl)naphthalene have been described recently[2-5]. These compounds can be regarded as phosphorus analogues of 1,8-bis(dimethylamino)naphthalene, known as "proton sponge"[6]. There is currently great interest in these new bisphosphanes as bidentate ligands possessing a rigid C_3-backbone, because the six-membered palladium(II) chelates that they form have been demonstrated to be active catalysts for CO/ethylene co-polymerization[3].

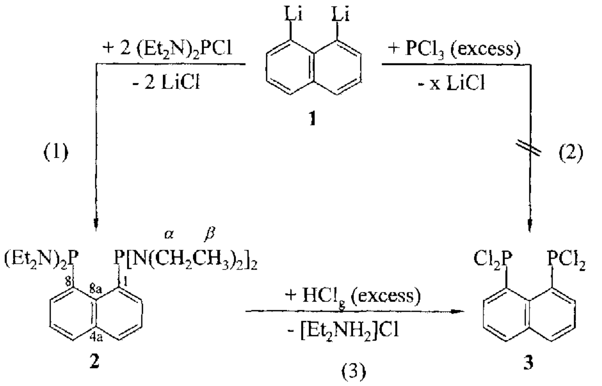
We now describe the first example of a 1,8-bis[(dialkylamino)phosphanyl]naphthalene, which can serve as a starting material for the synthesis of the hitherto unknown 1,8-bis(dichlorophosphanyl)naphthalene; the latter is not accessible by the direct route via the reaction of 1,8-dilithionaphthalene with phosphorus trichloride.

Results and Discussion

Treatment of 1,8-dilithionaphthalene **1**[7] with $(Et_2N)_2PCl$ in THF at −60°C gave 1,8-bis(diethylamino)phosphanyl]naphthalene **2** as a yellow oil (yield ca. 60%) which could not be obtained without traces of impurities (Scheme 1, eq. 1). Clear yellow crystals of **2** suitable for X-ray crystallography were grown from *n*-hexane at −20°C. When allowed to warm to room temperature the crystals melted to form a yellow oil.

The bis(aminophosphane) **2** was characterized by ^1H-, ^{13}C-, ^{31}P-NMR, and infrared spectroscopy, mass spectrometry, and a single-crystal X-ray diffraction study. Its δ_P value (+96.4) is typical of aryl-substituted bis(dialkylamino)phosphanes [cf. $PhP(NMe_2)_2$: δ_P = 100.3[8]].

Scheme 1. (1) THF, 1. −70 to −50°C; 2. room temp., 12 h. − (2) (2a) THF, −70 to −50°C or (2b) Et_2O, 0°C. − (3) 1. Et_2O, −80°C, 2. room temp., 12 h



Treatment of 1,8-dilithionaphthalene with PCl_3 in THF or diethyl ether at low temperature did not afford the expected bis(dichlorophosphane) **3** (Scheme 1, eq. 2). In each case pale yellow solids were obtained but could not be identified. These products were insoluble in all common polar and non-polar solvents, including boiling toluene. The reaction probably occurs via di- and trisubstitution at phosphorus leading to mixtures of oligomeric or polymeric products. Even variation of the reaction conditions did not prevent multiple substitution at phosphorus.

Because of the difficulty in introducing PCl_2 groups directly into the 1- and 8-position of naphthalene, protecting groups at phosphorus, such as dialkylamino groups, were

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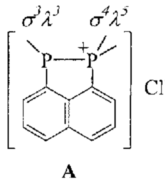
used. Cleavage of the P–N bond in (dialkylamino)phosphanes by HCl is a common synthetic method for chlorophosphanes[9]. Whereas diethylamino groups in simple aminophosphanes can easily be exchanged by chlorine, the close proximity of the substituents in **2** causes a complex and more complicated reaction pathway. Treatment of the bis(aminophosphane) **2** with gaseous HCl in diethyl ether gave the expected 1,8-bis(dichlorophosphanyl)naphthalene **3** in poor yield (9%), among other phosphorus-containing products (Scheme 1, eq. 3).

The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture showed, apart from numerous singlets, several AX spin systems containing pairs of doublets with coupling constants between 200 and 300 Hz, typical of $^1J(PP)$ coupling[10]. These AX spin systems probably represent ionic, PP'-bonded $[\sigma^3\lambda^3P\sigma^4\lambda^5P^+]$-diphosphorus compounds of the general structure **A** (Scheme 2):

Scheme 2

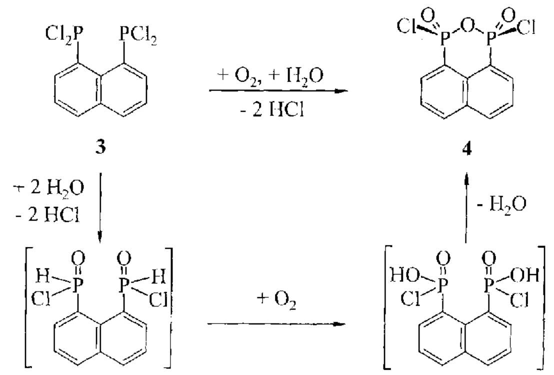


The characterization of the reaction products and the elucidation of the reaction mechanism are the subject of current studies. 1,8-Bis(dichlorophosphanyl)naphthalene **3** was isolated as a colourless solid which was characterized by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy, mass spectrometry, and elemental analysis. The $^{31}P\{^1H\}$-NMR spectrum showed a sharp singlet at $\delta_P = 135.7$. This remarkably high field shift value, compared to that of other aryl dichlorophosphanes [e.g. $PhPCl_2$: $\delta_P = 160$] could be explained by mutual shielding of the phosphorus nuclei, arising from the close proximity of the non-bonding electron pairs. The EI mass spectrum of **3** showed the molecular ion with the expected isotope pattern and peaks of higher intensities associated with the successive loss of chlorine.

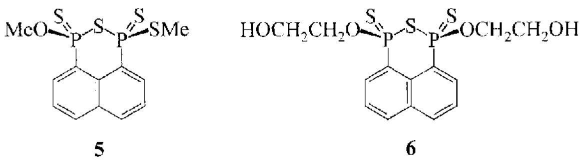
An attempt to recrystallize the bis(dichlorophosphane) **3** from dichloromethane/*n*-hexane in an NMR tube led to hydrolysis and apparent aerial oxidation with formation of **4**, an anhydride of a bis(chlorophosphonic acid). The product was identified by an X-ray structure analysis but the small amount available did not allow further characterization by spectroscopic methods or elemental analysis. The formation of **4** could be explained by the following mechanism in which the order of the consecutive reaction steps is not certain (Scheme 3).

Compound **4** resembles naphthalene derivatives containing C_3P_2S ring systems, such as **5** and **6**, which have been described by Woollins et al.[11,12] (Scheme 4). However, to the best of our knowledge **4** represents the first example of a cyclic compound containing the atom sequence P(:O)OP(:O) in a C_3P_2O ring, and only the second example of a structurally characterized C_3P_2O ring system[13].

Scheme 3



Scheme 4

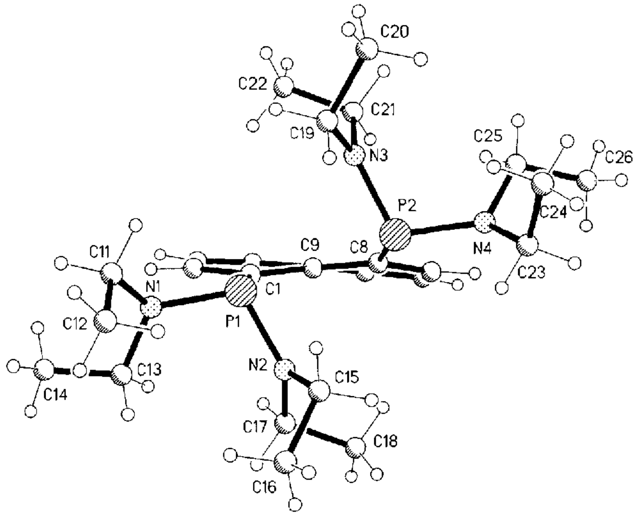


X-ray Investigations

The molecular structure of **2** is shown in Figure 1. The asymmetric unit consists of two independent molecules that are not significantly different from each other. A least-squares fit of the naphthalene carbon atoms gave a mean deviation of 2 pm; even the torsion angles of the ethyl groups are closely similar (Figure 2). Therefore, only one of the molecules is discussed in detail.

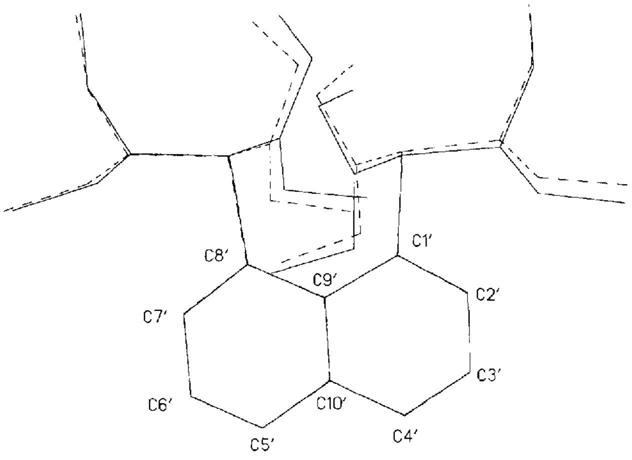
The most striking feature of the structure of **2** is the conformation of the $P(NEt_2)_2$ groups relative to the C_{10} plane. Whereas in alkyl- and aryl-substituted 1,8-bis(phosphanyl)-naphthalenes[3,5,14] the phosphanyl groups adopt a conformation between bisecting and eclipsed[15] (Scheme 5), the $P(NEt_2)_2$ groups in **2** prefer an almost eclipsed conformation. The corresponding torsion angles are 9° (N1–P1–C1–C2) and 4° (N4–P2–C8–C7). The substituents at P1 are directed to the opposite side of the C_{10} plane from those at P2. The orientation of the non-bonding electron pairs at phosphorus towards the C_{10} plane can be described by the pseudo torsion angles X–P1–C1–C2 and X–P2–C8–C7, where X is the centre of gravity of the atoms directly bonded to the corresponding phosphorus atom and P–X thus represents the opposite direction from the lone pair. The angles are 65° (X–P1–C1–C2), –116° (X–P1–C1–C9), 60° (X–P2–C8–C7), and –113° (X–P2–C1–C9); this indicates that the lone pairs are *gauche* with respect to the naphthalene framework. Similarly to other structures of 1,8-bis(phosphanyl)naphthalenes[3,5,14] the phosphanyl groups in **2** are bent *in-plane* and *out-of-plane*, leading to a non-bonding P1···P2 distance of 311.7 pm. The in-plane distortion takes the form of a widening of the bay angles P1–C1–C9, C1–C9–C8, and C9–C8–P2 to values as high as 126.1° for C1–C9–C8. Similar distortions were observed for 1,8-bis(dimethylphosphanyl)naphthalene[14] and other ditertiary 1,8-bis(phos-

Figure 1. Structure of one of the two independent molecules of **2** in the crystal viewed along the C9–C10 bond to emphasize the substituent orientation[a]

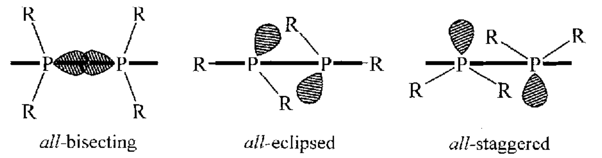


[a] Selected bond lengths [pm] and angles [°]: P(1)–N(2) 168.9(4), P(1)–C(1) 185.9(5), P(2)–N(4) 170.8(4), N(1)–C(11) 145.6(6), N(2)–C(17) 146.2(6), N(3)–C(19) 145.5(6), N(4)–C(23) 147.1(6), P(1)–N(1) 170.6(4), P(2)–N(3) 169.1(4), P(2)–C(8) 186.3(5), N(1)–C(13) 147.5(6); C(2)–C(1)–P(1) 118.0(4), C(9)–C(1)–P(1) 123.4(3), C(9)–C(8)–P(2) 122.5(3), C(7)–C(8)–P(2) 117.9(4), C(1)–C(9)–C(8) 126.1(4), N(2)–P(1)–N(1) 108.9(2), N(3)–P(2)–N(4) 109.5(2), N(3)–P(2)–C(8) 97.5(2), N(4)–P(2)–C(8) 101.1(2), C(11)–N(1)–P(1) 115.2(3), C(15)–N(2)–P(1) 116.4(3), P(1)–C(1)–C(8)–P(2) −24.8, P(1)–C(1)–C(9)–C(8) −8.97(66), P(2)–C(8)–C(9)–C(1) −20.48(64), N(1)–P(1)–C(1)–C(2) 9.3(4), N(4)–P(2)–C(8)–C(7) 4.5(4).

Figure 2. Superimposition of both independent molecules of **2** based on a least-squares fit of the naphthalene carbon atoms

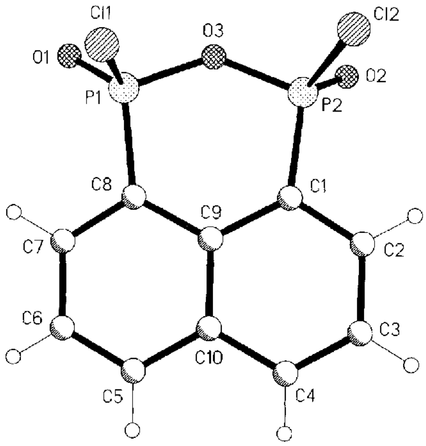


Scheme 5. Idealized conformations of 1,8-bis(phosphanyl)naphthalenes



phanyl)naphthalenes[3,5]. The out-of-plane distortion is quantified by the pseudo torsion angle P1–C1–C8–P2, which is −24.8°, and the displacement of P1 and P2 (by 42.7 and −76.5 pm) out of the best plane of the naphthalene ring. The latter is strongly distorted, the mean deviation from planarity (least squares) being 7.5 pm. The *ipso*-carbon atoms C1 and C8 are displaced by +14.5 and −20.2 pm above and below the mean C_{10} plane. Despite the steric congestion the phosphorus atoms in **2** display pyramidal geometry, with P–N bond lengths typical of aminophosphanes[16], whereas the environment of the nitrogen atoms is almost planar.

Figure 3. Structure of **4** in the crystal[a]



[a] Selected bond lengths [pm] and angles [°]: P(1)–O(1) 143.6(2), P(1)–C(8) 177.5(2), P(2)–O(2) 144.2(2), P(2)–C(1) 177.5(3), P(1)–O(3) 159.6(2), P(1)–Cl(1) 200.54(12), P(2)–O(3) 158.9(2), P(2)–Cl(2) 200.15(11); O(1)–P(1)–O(3) 110.30(12), O(1)–P(1)–C(8) 118.53(13), O(3)–P(1)–C(8) 104.71(11), O(3)–P(1)–Cl(1) 103.19(9), O(2)–P(2)–O(3) 110.15(12), O(2)–P(2)–C(1) 118.05(13), O(3)–P(2)–C(1) 105.87(11), P(2)–O(3)–P(1) 133.15(12), C(2)–C(1)–P(2) 115.5(2), C(8)–C(9)–C(1) 124.7.

Compound **4**, whose structure is shown in Figure 3, displays a phosphorus-containing heterocycle in which the P–O–P atom sequence, together with the three carbon atoms of the naphthalene framework, form a six-membered ring system. This six-membered ring exhibits a flattened boat conformation, in which the atoms P2, O3, C8, and C9 form a plane with a mean deviation of 0.8 pm. P1 (31.9 pm) and C1 (7.2 pm) lie outside of this plane. The naphthalene ring (mean deviation from planarity 1.9 pm) is less distorted in the phosphoryl compound **4** than in the aminophosphane **2**. The phosphorus atoms lie 19.7 pm (P1) and −26.4 pm (P2) outside the least squares plane of the naphthalene ring system, the torsion angle P2–C1–C8–P1 is −12.5° and the P1···P2 contact, now bridged via O3, is 292.3 pm. Similarly to **2**, in-plane distortion is indicated by a widening of the bay angles P1–C8–C9, C1–C9–C8, and C9–C1–P2 [123.1(2), 124.7(2), and 123.6(2)°]. The angle at the bridging oxygen [P1–O3–P2 133.15(12)°] is significantly larger than the "tetrahedral VSEPR value"[17], whereas the geometry at the phosphorus atoms may be described as distorted tetrahedral. The chloro substituents and the oxygen atoms are arranged *cis* with respect to the ring. The P–C [177.5(3) pm], P–Cl [200.54(12) and 200.15(11) pm], P–O [159.6(2) and 158.9(2) pm] and P=O

[143.6(2) and 144.2(2) pm] bond lengths are in the usual range[16].

The relief of strain in **4** is a consequence of the removal of the repulsive lone-pair interaction that exists in 1,8-bis(phosphanyl)naphthalenes and the concomitant introduction of the bridging oxygen atom. Pringle et al.[18] observed the same effect when they compared the structure of 1,8-bis(diphenylphosphanyl)naphthalene coordinated to a palladium(II) fragment with that of the free ligand. This behaviour is directly analogous to the structural changes that occur when proton sponge is protonated, the loss of strain energy accounting for the remarkably high basicity of the latter[18].

Conclusion

Our studies of derivatives of 1,8-bis(phosphorus) substituted naphthalenes have given access to a bis(dichlorophosphane) and an anhydride of a bis(chlorophosphonic acid) by P−N bond cleavage of the corresponding diethylaminophosphane with HCl gas, followed by oxidative hydrolysis. The syntheses described here afford the desired products only in poor yields. Current investigations are focussing on related compounds as precursors for the synthesis of 1,8-bis(dichlorophosphanyl)naphthalene, which is expected to be a versatile ligand in coordination chemistry and which is also expected to exhibit interesting main group chemistry.

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Experimental Section

All experiments were carried out with exclusion of air and moisture, solvents were purified and dried according to the usual methods[19]. In vacuo (i. v.) refers to a pressure of 0.05 Torr at 25°C. − NMR: Bruker AC-200 (^{1}H: 200.1 MHz, ^{13}C: 50.3 MHz, ^{31}P: 81.0 MHz) and Bruker AM-400 (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz), reference substances were $SiMe_4$ (TMS) (int.) or (indirectly) $CHCl_3$ at $\delta_H = 7.25$ and $\delta_C = 77.05$, and C_6D_6 at $\delta_H = 7.15$ and $\delta_C = 128.00$ (^{1}H, ^{13}C), and 85% H_3PO_4 (ext.) (^{31}P); high-field shifts are given negative, low-field shifts positive signs; m_c denotes a complex multiplet. − MS (70 eV): Finnigan MAT 8430. − IR: Nicolet 320 FT-IR spectrometer. − Elemental analyses: Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig. − The melting point was determined on a Büchi 530 melting point apparatus using a sealed 0.1 mm capillary tube and is uncorrected. − 1,8-Dilithionaphthalene[7] and bis(diethylamino)chlorophosphane[9] were prepared as described in the literature. All other reagents were obtained commercially.

1,8-Bis[(diethylamino)phosphanyl]naphthalene (**2**): A suspension of 1,8-dilithionaphthalene (**1**) in 20 ml of THF, prepared from 4.14 g (20.0 mmol) of 1-bromonaphthalene, was cooled to −70°C and a solution of 10.54 g (50.0 mmol) of bis(diethylamino)chlorophosphane in 10 ml of THF was added. The reaction mixture was allowed to warm to room temp. and was stirred 12 h, whereby a brown solid and a red solution were formed. The solvent was removed i. v., the residue was extracted with 50 ml of *n*-hexane and the insoluble lithium salts were separated by filtration. The solvent and all volatile components were removed i. v. at 80°C and 10.15 g of a wine-red viscous product were obtained. The crude product was dissolved in the minimum amount of *n*-hexane and was stored at −20°C, whereby yellow crystals were formed after 2 d which were washed three times with 5 ml portions of acetonitrile. The crystals melted when warmed to room temp. to give a yellow viscous product (5.70 g, 12 mmol, 60%). Even repeated recrystallization from *n*-hexane did not afford compound **2** free from traces of impurities. Some of the crystals were suitable for an X-ray structure analysis at low temperature. − ^{1}H NMR (C_6D_6): $\delta = 0.92$ [t, $^3J(^{\alpha}H^{\beta}H) = 7.0$ Hz, 24H, NCH_2CH_3], 2.96 [m_c, 16H, NCH_2CH_3], 7.36 [m_c ($\approx$ t), $^3J(HH) \approx 7.5$ Hz, 2H, 3-H], 7.64 [m_c ($\approx$ dd), $^3J(^3H^4H) \approx 8.0$ Hz, $^4J(^2H^4H) \approx 1.3$ Hz, 2H, 4-H], 7.96 [m_c ($\approx$ dd) (br), $^3J(^2H^3H) \approx 7.0$ Hz, $^4J(^2H^4H) \approx 1.6$ Hz, 2H, 2-H]. − ^{13}C NMR (C_6D_6): $\delta = 14.65$ [s, NCH_2CH_3, C-β], 43.63 [t, $J = 10.9$ Hz, NCH_2CH_3, C-α], 124.04 [s, C-3,6], 129.73 [s, C-4,5], 130.28 [m_c ($\approx$ t), $J \approx 3.4$ Hz, C-2,7], 134.90 [m_c ($\approx$ t), $J \approx 17.3$ Hz, C-8a], 135.55 [m_c ($\approx$ t), $J \approx 2.2$ Hz, C-1,8], 143.09 [t, $J = 19.3$ Hz, C-4a]. − $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = +96.4$ [s]. − IR (film): $\tilde{\nu}$ (cm^{-1}) = 3048 (w), 2965 (s), 2929 (m), 2854 (m), 2361 (w), 2341 (w), 1459 (m), 1374 (s), 1292 (w), 1187 (sst), 1030 (s), 1013 (s), 907 (m, br), 821 (w), 791 (m), 774 (m), 661 (m). − EI-MS (70 eV): *m/z* (%) = 476 (0.9) [M^+], 404 (100) [$M^+ - N(C_2H_5)_2$], 332 (12) [$M^+ - 2\ N(C_2H_5)_2$], 302 (24) [$M^+ + H - P\{N(C_2H_5)_2\}_2$], 277 (44), 230 (52) [$M^+ + H - N(C_2H_5)_2 - P\{N(C_2H_5)_2\}_2$], 175 (60) [$P\{N(C_2H_5)_2\}_2$]$^+$, 72 (96) [$N(C_2H_5)_2$]$^+$. − [$C_{26}H_{46}N_4P_2$ (476.62)].

1,8-Bis(dichlorophosphanyl)naphthalene (**3**): A solution of 7.0 g (14.7 mmol) of bis(aminophosphane) **2** in 50 ml of diethyl ether was placed into a 100-ml two-necked flask, equipped with a bubbler. The solution was cooled to −80°C and was saturated with gaseous HCl. The reaction mixture was allowed to warm to room temp., was stirred for 3 h and was investigated by $^{31}P\{^1H\}$-NMR spectroscopy. After stirring for another 12 h at room temp. the reaction mixture was worked up. The precipitate of diethylamine hydrochloride was separated and the solvent was removed in vacuo. The residue was washed with 5 ml of *n*-hexane and was investigated by $^{31}P\{^1H\}$-NMR spectroscopy. The product was obtained as a colourless, crystalline solid (m.p. 107°C) by threefold recrystallization from dichloromethane/*n*-hexane at −20°C (0.480 g, 1.45 mmol, 9%). − ^{1}H NMR ($CDCl_3$): $\delta = 7.72$ [m_c ($\approx$ t), $^3J(HH) \approx 7.7$ Hz, 2H, 3-H], 8.05 [m_c ($\approx$ dd), $^3J(^3H^4H) \approx 8.2$ Hz, $^4J(^2H^4H) \approx 0.9$ Hz, 2H, 4-H], 8.67 [m_c ($\approx$ dq) (br), $^3J(^2H^3H) \approx 7.2$ Hz, $^4J(^2H^4H) \approx 1.2$ Hz, 2H, 2-H]. − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 135.7$ [s]. − EI-MS (70 eV): *m/z* (%) = 328 (8) [M^+], 293 (100) [$M^+ - Cl$], 258 (24) [$M^+ - 2\ Cl$], 239 (16), 223 (30) [$M^+ - 3\ Cl$], 192 (10), 188 (38) [$M^+ - 4\ Cl$], 157 (77) [$M^+ - 2\ Cl - PCl_2$]. − $C_{10}H_6Cl_4P_2$ (329.92): calcd. C 36.41, H 1.83; found C 36.26, H 1.76.

1,3-Dichloro-2,3-dihydro-1,3-dioxo-2-oxa-1,3-diphosphaphenalene (**4**): A saturated solution of 1,8-bis(dichlorophosphanyl)naphthalene (**3**) in dichloromethane/*n*-hexane was left in an NMR tube at room temp. After three days colourless crystals suitable for X-ray diffraction studies were formed, which proved to be the heterocyclic compound **4** [$C_{10}H_6Cl_2O_3P_2$ (307.01)].

Crystal-Structure Analyses: Crystal data: **2**, $C_{26}H_{46}N_4P_2$, $M = 476.61$, yellow tablet, 0.80 × 0.30 × 0.15 mm, monoclinic, space group $P2_1/c$, $a = 1777.1(4)$, $b = 1753.7(4)$, $c = 1781.2(4)$ pm, $\beta = 92.37(3)°$, $V = 5.546(2)$ nm^3, $Z = 8$, $D_X = 1.142$ Mg m^{-3}, λ (Mo-K_{α}) = 71.073 pm, $F(000) = 2080$, $T = -130°C$, $\mu = 0.177$ mm^{-1}, number of reflections: 11612 (9777 independent, $R_{int} = 0.060$), $R(F) = 0.075$, $wR(F^2) = 0.151$, $\Delta\rho_{max} = 474$ e nm^{-3}, $\Delta/\sigma < 0.001$; **4**, $C_{10}H_6Cl_2O_3P_2$, $M = 306.99$, colourless tablet, 0.65 × 0.60 ×

0.10 mm, triclinic, space group $P\bar{1}$, a = 804.3(2), b = 813.0(2), c = 986.1(2) pm, α = 67.64(2), β = 84.161(14), γ = 76.10(2)°, V = 0.5789(2) nm^3, Z = 2, D_X = 1.761 Mg m^{-3}, λ (Mo-K_α) = 71.073 pm, $F(000)$ = 308, T = −100°C, μ = 0.826 mm^{-1}, Absorption correction: ψ scans, min. trans. = 0.720, max. trans. = 0.936, number of reflections: 3256 (2549 independent, R_{int} = 0.013), $R(F)$ = 0.042, $wR(F^2)$ = 0.116, $\Delta\rho_{max}$ = 763 e nm^{-3}, $\Delta/\sigma < 0.001$. – Data collection and reduction: Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 for **2** and Siemens **P4** for **4**, both with LT-2 low temperature attachment). The cell constants for **2** were refined from ±ω angles of 52 reflections in the 2Θ range 20–23°. The orientation matrix for **4** was refined from setting angles of 62 reflections in the 2Θ range 5–25° (monochromated Mo-K_α radiation). – Structure solution and refinement: The structures were solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-93, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. The weighting scheme was of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$.

Full details of the crystal structure determinations (except structure factors) have been deposited under the number CCDC-100293 at the Cambridge Crystallographic Data Centre. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (Fax: internat. +44(0)1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk).

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☆ Dedicated to Professor *Hans Bürger* on the occasion of his 60th birthday.