0.031 g, 18%. IR (Nujol, Fluorolube): $\tilde{\nu}$ = 2923 (s), 2853 (m), 1450 (m), 1372 (w), 1242 (w), 1192 (m), 1116 (m), 1060 (s), 1029 (m), 861 cm^{-1} (m).

The dark blue mother liquor from above was stored at −20 °C for 24 h to yield a second crop of purple crystals, however this time of **2**. The crystals were washed with DME (2 × 1 mL) and dried briefly under vacuum. Yield: 0.034 g, 19%. IR (Nujol, Fluorolube): $\tilde{\nu}$ = 3009 (w), 2925 (s), 2828 (m), 1455 (s), 1365 (w), 1241 (w), 1191 (m), 1114 (s), 1064 (s), 1027 (s), 860 (m), 722 cm^{-1} (w).

Under argon, crystals of **1** and **2** decompose without melting above 200 °C, but are stable without loss of DME at ambient temperature for extended periods of time. In air, decomposition is remarkably slow; the crystals are covered with a thin layer of yellow Sm^{III} only after several minutes. Both **1** and **2** are virtually insoluble in diethyl ether and toluene; the solubility in DME is approximately 0.01M.

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[10] If sonication using an ordinary cleaning bath is applied, samarium chips can be used instead of the more expensive samarium powder.
[11] Crystal structure data for Λ-**1** ($SmI_2O_6C_{12}H_{30}$): crystal size 0.1 × 0.1 × 0.1 mm, monoclinic, space group $P2_1$ (no. 4), a = 8.4797(15), b = 10.601(3), c = 12.3120(15) Å, β = 93.743(12)°, V = 1104.4(4) Å^3, Z = 2, ρ_{calcd} = 2.028 g cm^{-3}, $2\theta_{max}$ = 50.0°, $Mo_{K\alpha}$ radiation, $\omega/2\theta$ scan mode, T = −130 °C, psi scans (abs. range 0.915 – 0995), μ = 5.47 mm^{-1}. Refinement on F^2 for 2060 reflections and 196 parameters gave $R1$ = 0.023 and $wR2$ = 0.060 for $I > 2.0\sigma(I)$. The Sm, I, O, and C atoms were refined with anisotropic thermal displacement parameters, and the H atoms were included in calculated positions and allowed to ride on their respective carbon atom during refinement; max./min. residual electron density 0.56/ − 0.59 e Å^{-3}; Flack parameter − 0.02(3). Crystals of Δ-**1** gave similar data. Crystal structure data for **2** ($SmI_2O_6C_{12}H_{30}$): crystal size 0.2 × 0.1 × 0.1 mm, monoclinic, space group $C2/c$ (no. 15), a = 25.059(7), b = 13.157(4), c = 14.598(6) Å, β = 115.74(2)°, V = 4335(3) Å^3, Z = 8, ρ_{calcd} = 2.067 g cm^{-3}, $2\theta_{max}$ = 50.0°, $Mo_{K\alpha}$ radiation, $\omega/2\theta$ scan mode, T = −130 °C, psi scans (abs. range 0.777 – 0998), μ = 5.575 mm^{-1}. Refinement on F^2 for 3818 reflections and 186 parameters gave $R1$ = 0.041 and $wR2$ = 0.11 for $I > 2.0\sigma(I)$. The Sm, I, O, and ordered C atom were refined with anisotropic thermal displacement parameters, while the disordered C atoms were refined isotropically with the SOFs fixed to 0.5. The H atoms were refined with the riding model, but the H atoms on the disordered C atoms were not located; max./min. residual electron density 1.48/ − 1.61 e Å^{-3}. Both structures were solved using SHELXS and refined using SHELXL-97. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114182 (Λ-**1**) and CCDC-114183 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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New Types of Stable Aldehydes: Formylphosphane and Formylphosphane Oxide**

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Very few stable derivatives featuring the formyl group directly bound to a heavy Group 14 or 15 element have previously been prepared. Only two formylsilanes have been isolated.[1] Although β-, γ-, and ω-phosphorylated aldehydes are popular reagents,[2] α-phosphorus-substituted aldehydes have not even been spectroscopically characterized.[3] In contrast, several stable masked derivatives are known,[4] the formylphosphonic acid hydrate even being an antiviral agent.[5] Here we report the synthesis and characterization of the formylphosphanes **2a, b** and formylphosphane oxide **4** (see Scheme 1); the crystal structure of **2b** is also presented.

Treatment of the iminium salts **1a, b**[6] with a suspension of KOH in thf at room temperature affords the desired formylphosphanes **2a, b**, which were isolated as a yellow oil (78% yield) and white crystals (82% yield), respectively (Scheme 1). The ^{31}P NMR signal for the formylphosphane **2a** is a doublet at δ = 68.1 with a remarkably large phosphorus – proton coupling (^2J(P,H) = 84 Hz).[7, 4d] Interestingly, the ^{1}H (δ = 11.1) and ^{13}C NMR signals (δ = 220.1, ^1J(P,C) = 17 Hz) for the formyl group appear at rather low field, and the ν(CO) IR stretching frequency at 1668 cm^{-1} is unusually low for an aldehyde.

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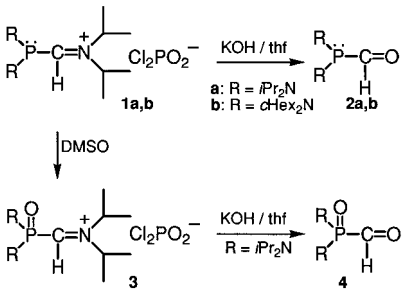


Scheme 1. Synthesis of formylphosphanes **2a, b** and formylphosphane oxide **4**.

The molecular structure[8] of **2b** is shown in Figure 1. The phosphorus atom is in a pyramidal environment (sum of the three bond angles 314°), and the P1–C1 (1.841 Å) and C1–O1

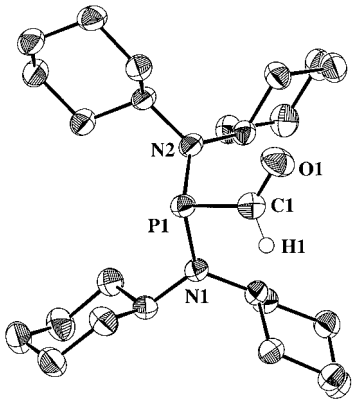
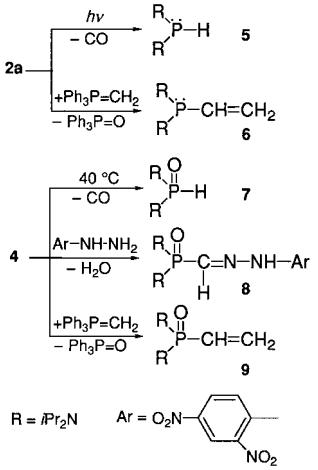


Figure 1. Molecular structure of **2b**. Selected bond lengths [Å] and angles [°]: P1–N1 1.684(2), P1–N2 1.671(2), P1–C1 1.841(2), C1–O1 1.214(3); N1-P1-N2 113.89(10), N1-P1-C1 97.25(11), N2-P1-C1 103.18(10), P1-C1-O1 125.3(2).

bond lengths (1.214 Å) are in the range expected for P–C single and C–O double bonds. These structural data confirm the absence of any interaction between the phosphorus lone pair and the carbonyl group. This is in agreement with the high inversion barrier of phosphanes (compared to amines), which inhibits the "inherent" π donor capabilities of phosphorus.[9]

The formylphosphanes **2a, b** are remarkably stable: No noticeable decomposition was observed upon refluxing in toluene for three days. However, as for classical aldehydes, **2a** undergoes a smooth decarbonylation under photolysis (254 nm), and the diaminophosphane **5**[10] was obtained in almost quantitative yield (Scheme 2).

The thermal stability of **2** prompted us to try synthesizing the corresponding formylphosphane oxide **4**. Oxidation of the iminium salt **1a** with excess dimethylsulfoxide (acetonitrile, 50 °C, 4 h) led to **3** (60 % yield). Subsequent treatment with a suspension of KOH in thf at room temperature afforded the desired aldehyde **4**, which was isolated as a yellow oil in 78 % yield (Scheme 1). The spectroscopic data for the formyl group of **4** ($\delta(^1H) = 10.6$, $^2J(P,H) = 110$ Hz; $\delta(^{13}C) = 210.4$, $^1J(P,C) = 132$ Hz; $\tilde{\nu}(CO) = 1697$ cm^{-1}) are very similar to those of the corresponding formylphosphanes **2** (it is well known that J(P,C) increases with the coordination number of P). However, **4** is by far less thermally stable than **2**, since it slowly looses CO at 40 °C,[11] quantitatively giving the phosphane oxide **7** (Scheme 2).



Scheme 2. Some reactions of formylphosphanes **2a, b** and formylphosphane oxide **4**.

Since there is no π interaction between the phosphorus lone pair and the C–O double bond, the phosphanyl group of **2** acts as a σ-donor substituent. In contrast, the phosphoranyl group of **4** is expected to act as a σ- and π-acceptor substituent. The different electronic properties of the two phosphorus-containing substituents might explain the relative instability of **4** compared to **2**, and suggest a higher electrophilicity for **4**.

Indeed, the reactivities of **2a** and **4** appear to be somewhat different (Scheme 2). No reaction was observed when 2,4-dinitrophenylhydrazine was added to **2a**, whereas **4** readily reacted to give the corresponding hydrazone **8** (50 % yield). However, both **2a** and **4** react with stronger nucleophiles such as methylenetriphenylphosphorane[12] to afford the corresponding olefins **6** and **9** in good yields.

Experimental Section

General procedure for the preparation of aldehydes: To a solution of the iminium salts **1** or **3** (3 mmol) in thf (10 mL) was added at room temperature a suspension of dry KOH (0.18 g, 3.2 mmol) in thf (5 mL). The solution mixture instantaneously turned bright yellow, and ^{31}P NMR spectroscopy indicated the quantitative formation of the corresponding aldehyde.

2a: $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 24.3$ (d, $^3J(P,C) = 5.9$ Hz, PNCHCH_3), 24.9 (d, $^3J(P,C) = 6.4$ Hz, PNCHCH_3), 50.6 (d, $^2J(P,C) = 9.3$ Hz, PNCH), 220.1 (d, $^1J(P,C) = 17.0$ Hz, C=O); ^{1}H NMR (C_6D_6): $\delta = 1.14$ (d, 12 H, $^3J(H,H) = 6.6$ Hz, CH_3), 1.27 (d, 12 H, $^3J(H,H) = 6.6$ Hz, CH_3), 3.18 (sept d, 4 H, $^3J(H,H) = 6.6$ Hz, $^3J(P,H) = 11.4$ Hz, NCH), 11.14 (d, 1 H, $^2J(P,H) = 84.0$ Hz, HC=O); IR (C_6D_6): $\tilde{\nu} = 2725$ (CH), 1668 cm^{-1} (C=O).

2b: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 76.0$; $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 25.1$, 25.5, 26.5, 26.6 (s, CH_2), 34.8 (d, $^3J(P,C) = 5.0$ Hz, CH_2), 35.6 (d, $^3J(P,C) = 5.7$ Hz, CH_2), 59.8 (br s, PNCH), 222.3 (d, $^1J(P,C) = 20.0$ Hz, C=O); ^{1}H NMR (C_6D_6): $\delta = 10.87$ (d, 1 H, $^2J(P,H) = 88.1$ Hz, CH=O); IR (C_6D_6): $\tilde{\nu} = 2853$ (CH), 1654 cm^{-1} (C=O).

3: M.p. 148–150 °C; $^{31}P\{^1H\}$ NMR (CD_3CN): $\delta = 9.5$, −9.4 ($Cl_2PO_2^-$); $^{13}C\{^1H\}$ NMR (CD_3CN): $\delta = 175.5$ (d, $^1J(P,C) = 20.5$ Hz, C=N); ^{1}H NMR (CD_3CN): $\delta = 8.42$ (d, 1 H, $^2J(P,H) = 17.5$ Hz, CH=N).

4: $^{31}P\{^1H\}$ NMR (CD_3CN): $\delta = 11.6$; $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 22.9$ (s, CH_3), 45.7 (d, $^2J(P,C) = 9.3$ Hz, PNCH), 210.4 (d, $^1J(P,C) = 131.8$ Hz, C=O); ^{1}H NMR (C_6D_6): $\delta = 1.14$ (d, 12 H, $^3J(H,H) = 6.8$ Hz, CH_3), 1.21 (d, 12 H, $^3J(H,H) = 6.8$ Hz, CH_3), 3.33 (sept d, 4 H, $^3J(H,H) = 6.8$ Hz, $^3J(P,H) = 16.2$ Hz, NCH), 10.60 (d, 1 H, $^2J(P,H) = 110.0$ Hz, CH=O); IR (C_6D_6): $\tilde{\nu} = 2732$ (CH), 1697 cm^{-1} (C=O).

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8: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 17.0$; $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 147.8$ (d, $^1J(P,C) = 113.2$ Hz, P–CH=N); ^1H NMR ($CDCl_3$): $\delta = 7.23$ (d, 1H, $^2J(P,H) = 40.0$ Hz, CH=N).

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[8] Crystal data for **2b**: $C_{25}H_{45}N_2OP$, $M_r = 420.60$, monoclinic, space group $P2_1/n$, $a = 11.105(1)$, $b = 11.332(2)$, $c = 20.194(2)$ Å, $\beta = 103.57(1)^\circ$, $V = 2470.3(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.131$ Mg m^{-3}, $F(000) = 928$, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\mu(Mo_{K\alpha}) = 0.129$ mm^{-1}, crystal size $0.6 \times 0.5 \times 0.1$ mm, $2.07^\circ < \Theta < 23.26^\circ$; 17819 reflections (3432 independent, $R_{int} = 0.116$) were collected at low temperatures using an oil-coated shock-cooled crystal[13] on a STOE-IPDS diffractometer. A numerical absorption correction was employed, and the min./max. transmissions are 0.7441 and 0.9559. The structure was solved by direct methods (SHELXS-97[14]), and 266 parameters were refined using the least-squares method on F^2.[15] Largest residual electron density 0.203 e Å^{-3}, $R_1 = 0.047$ (for $F > 2\sigma(F)$) and $wR_2 = 0.121$ (all data) with $R_1 = S||F_o| - |F_c||/S|F_o|$ and $wR_2 = (Sw(F_o^2 - F_c^2)^2/Sw(F_o^2)^2)^{0.5}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116054. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Convergent Strategy for the Modification of Peptide Nucleic Acids: Novel Mismatch-Specific PNA-Hybridization Probes**

Oliver Seitz,* Frank Bergmann, and Dieter Heindl

Medicinal applications such as gene therapy as well as gene diagnostics greatly benefit from synthetic compounds that sequence-specifically recognize and bind nucleic acids.[1] Peptide nucleic acids (PNAs) represent a promising class of DNA analogues in which the entire sugar – phosphate backbone is replaced by a pseudopeptide backbone.[2] Their successful use as hybridization probes fuels research that is aimed at the development of new polyamide-based DNA binders.[2d] However, little attention is directed towards the elaboration of techniques to site-specifically modify PNA oligomers, although the feasibility to serve as hybridization probe relies on the selective introduction of reporter groups. In all studies to date, nonstandard nucleobases were incorporated by coupling of the corresponding monomeric building blocks.[2d, 3] A strategy in which the modified nucleobases are coupled to an orthogonally protected backbone on solid phase would omit the need to synthesize an entire monomer in solution.[4] Thus, the rapid synthesis and the efficient screening of modified PNA conjugates would be greatly facilitated. This work presents a convergent strategy to selectively functionalize and label PNA at terminal as well as internal positions.

The central building block for the "on-resin synthesis" of nonstandard PNA monomers is the orthogonally protected aminoethylglycine **1** (Scheme 1).[5] For validation, the building block **1** was conjugated to the allylic HYCRON linker, which provides orthogonal stability in combination with commonly used protecting-group strategies.[6] The aminoethylglycine – HYCRON conjugate **3** was synthesized by allowing the Boc/Fmoc-protected PNA backbone **1** to react with the allylic bromide **2** followed by the reductive removal of the phenacyl ester moiety. The Boc/Fmoc-protected conjugate **3** was attached to the resin using HBTU and HOBt. Treatment of **4** with DMF/morpholine liberated a compound with a secondary amino group, which subsequently was subjected to a coupling reaction with **5**. In the presence of the allyl scavenger morpholine, resin **6** was treated with catalytic amounts of the Pd^0 catalyst $[Pd(PPh_3)_4]$. The Boc/Z-protected guanosine analogue **7** was obtained in a yield of 61 % based on the initial load of resin **4** with Fmoc groups. A comparison with the 70 – 80 % yield of the corresponding solution synthesis illustrates the efficiency of this on-resin synthesis of the protected PNA-monomer **7**.[7, 8]

As part of our research on new assays for the real-time detection of oligonucleotide hybridization of an oligomer, we

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