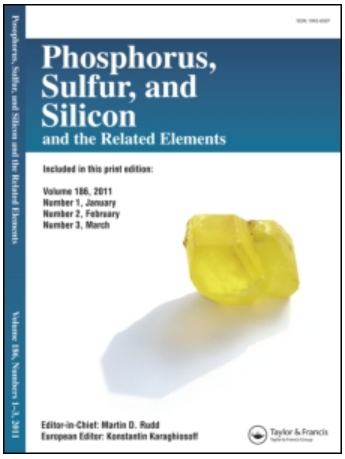

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Hydrido-bis(*meso*-oxolanylen-3,4-dioxy)-λ⁵-phosphane

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Hydrido-bis(*meso*-oxolanylen-3,4-dioxy)-λ^5-phosphane

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*The symmetric hydrido-spiro-λ^5-phosphane derived from anhydroerythritol (*meso*-oxolane-3,4-diol, AnEryt), HP(AnErytH$_{-2}$)$_2$(**3**), was prepared by two different synthetic protocols. One route involves a three step synthesis starting from phosphorus trichloride via 2-chloro-tetrahydro-furo[3,4-*d*][1,3,2]dioxaphosphole (**1**) and diethyl-(tetrahydro-furo[3,4-*d*][1,3,2]dioxaphosphol-2-yl)-amine (**2**) as intermediates. The first intermediate, P(AnErytH$_{-2}$)Cl (**1**), was isolated as a crystalline solid and its structure was determined by single crystal X-ray diffraction. **1** is the first example of a halogeno substituted phosphane derived from an aliphatic diol whose molecular structure in the solid state was determined by X-ray diffraction studies. Alternatively, the title compound can also be obtained in a one-pot procedure starting from tris(*N,N*-dimethylamino)phosphane. All new compounds were characterized by their physical constants (melting point, refractory index), NMR, IR, Raman, UV/VIS, mass spectrometry, as well as elemental analysis. Some spectroscopic proofs for the spiro nature of the title compound are given.*

Keywords Alkylenedioxyphosphane; crystal structure; phosphorus; spiro compounds

INTRODUCTION

Phosphorus plays a key role in biochemistry as important part of the desoxyribonucleid acid, adenosine triphosphate and many other compounds in living organisms. The metabolism of nutrients involves several phosphorylation steps.[1] Based on the work of Westheimer et al.,[2,3] the possible intermediacy of a pentavalent phosphorus during phosphoryl transfer reactions has been extensively discussed in the literature,[4,5] and recently, the structure of an intermediate from

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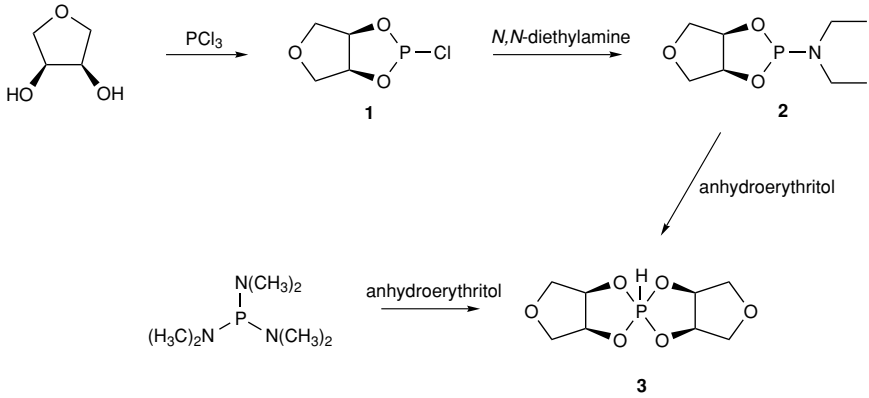
a phosphoryl transfer reaction containing a pentacoordinate phosphorus atom was elucidated by means of a single crystal X-ray study.[6] Being ubiquitous in cellular environments, carbohydrates appear as attractive bonding partners for pentavalent phosphorus. However, a definite proof for the structure of such compounds based on data obtained from single crystal X-ray experiments was lacking completely in the literature up to some years ago. Important progress in solving this problem was achieved by Holmes and co-workers by incorporation of the phosphorus atom into a macrocyclic framework. Consequently, a series of carbohydrate-substituted λ^5-phosphoranes with protected glucofuranoside and xylofuranoside, β-chloralose and thymidine, was investigated by single crystal X-ray diffraction showing for some of these compounds formal hexacoordination by intramolecular donor interaction.[7–9] However, symmetric λ^5-phosphanes bearing two carbohydrate moieties are still unknown. Additionally, to faciliate bonding of carbohydrates to phosphorus it would be desirable for the fifth substituent at phosphorus to have a low steric demand. Pursuing the latter strategy, hydrido-spiro-λ^5-phosphanes appear to be particularly suitable for this purpose. This class of molecules has attracted some attention during the 1960s and 1970s,[10–12] but has been observed only for a limited number of almost exclusively open-chain diols (except *cis*-cyclohexane-1,2-diol[13]) leaving the question about the possible extension to carbohydrates as chelating partners unanswered. To test whether hydrido-spiro-λ^5-phosphanes might, in principle, be formed with carbohydrates, anhydroerythritol—a vicinal diol representing a model for furanoid carbohydrates containing *cis*-configured hydroxyl groups—was used as a starting material. As of today, only two structures of hydrido-spiro-λ^5-phosphanes resulting from vicinal diols (pyrocatechol[14] and 2,3-diphenylethane-1,2-diol[15]) have been elucidated by means of single crystal X-ray diffraction.

RESULTS AND DISCUSSION

The synthesis of the hydrido-spiro-λ^5-phosphane with anhydroerythritol as the chelating diol was performed according to two different synthetic protocols described in the literature[12,16] in a three-step sequence starting from phosphorus trichloride and in one step starting from tris(*N*,*N*-dimethylamino)phosphane (Scheme 1). Despite of the three steps the first reaction sequence is of interest since exclusively cheap starting materials are involved.

2-Chloro-tetrahydro-furo[3,4-*d*][1,3,2]dioxaphosphole, P(AnErytH$_{-2}$)Cl (**1**), was obtained by reaction of anhydroerythritol with phosphorus trichloride in dichloromethane. It was isolated as a liquid, which



SCHEME 1 Routes for the preparation of the symmetric hydrido-spiro-λ⁵-phosphane **3** derived from anhydroerythritol.

crystallizes on prolonged storage at room temperature. The results of a single crystal X-ray study prove phosphorus to be part of a five-membered chelate ring (Figure 1). The phosphorus atom is found at the top of a trigonal pyramid. Bond lengths and angles around the phosphorus atom are in good agreement with the values reported in the literature for similar compounds derived from aromatic hydroxycarboxylic acids or aromatic diols.[17–25] A puckering analysis of the five-membered rings according to Cremer and Pople shows the chelate ring, as well as

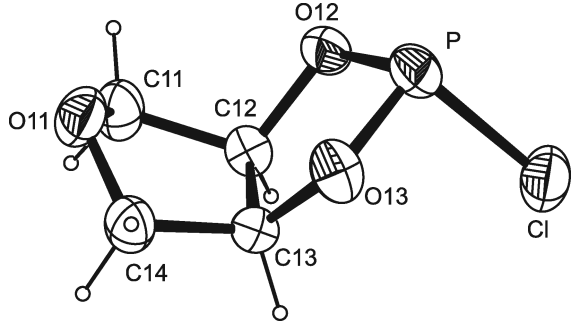


FIGURE 1 Molecular structure of P(AnErytH$_{-2}$)Cl(**1**) (50% probability ellipsoids). Selected distances (in Å) and angles (in °): Cl–P 2.1152(7), P–O13 1.6008(13), P–O12 1.6041(13), O12–C12 1.4459(18), O13–C13 1.4511(19), C12–C13 1.542(2), O13–P–O12 95.48(6), O13–P–Cl 100.10(5), O12–P–Cl 99.90(5), C12–O12–P 112.82(9), C13–O13–P 112.99(9), O12–C12–C13–O13 −0.22(16); ring puckering analysis [9]: P–O12–C12–C13–O13 Q_2= 0.2325(12) Å, φ_2= 0.4(4)° (*envelope* on P); O11–C11–C12–C13–C14 Q_2= 0.3840(17) Å, φ_2= 0.9(3)° (*envelope* on O11).

the oxolane ring to adopt an *envelope* conformation.[26] The oxolane moiety is oriented away from the chlorine atom and *syn* to the free electron pair at phosphorus.

A solution of crystals of **1** in $CDCl_3$ shows two signals in the ^{31}P NMR spectrum and two sets of signals in the ^{13}C NMR spectrum, which is in accordance with the two possible stereoisomers (*syn* and *anti*) for **1**. According to integration of the ^{31}P NMR signals the relative ratio of the two isomers is about 30:1. A comparison between the carbon resonances of anhydroerythritol and the corresponding signals in the ^{13}C NMR spectrum of **1** shows that the signal of the CH groups of the latter in the case of the minor isomer are shifted by 13.4 ppm downfield. For the major isomer the downfield shift of these carbon atoms is with 11.4 ppm less pronounced. No shift difference for the two isomers is observed for the resonances attributable to the methylene groups. The ^{31}P NMR resonances at 183 ppm (minor isomer) and 175 ppm (major isomer) are typical for trivalent phosphorus compounds of this type.[27] The proton spectrum of **1** shows the expected high order line pattern for the ABM-part of an $[ABM]_2X$ spin system.

The compound is highly reactive and decomposes rapidly with evolution of white fumes upon exposure to air or moisture.

To avoid halogenido-induced side reactions during the formation of the desired hydrido-spiro-λ^5-phosphane, the remaining chlorine atom at phosphorus was substituted for another appropriate leaving group. Reaction of **1** with *N*, *N*-diethylamine in an aprotic solvent yielded the amino substituted derivative **2**, which was isolated by distillation. The liquid showed no tendency to crystallize at room temperature even after a storage period of more than 18 months. The ^{31}P, ^{13}C, ^{1}H, and ^{15}N NMR spectra of **2** display each two sets of signals (ratio approximately 1:8), which suggests the presence of a *syn* and an *anti* isomer. A comparison of the ^{13}C NMR chemical shifts of **2** with those of neat anhydroerythritol shows for the CH carbon atoms in **2** a downfield shift of 8.0 ppm (main isomer) and of 7.4 ppm (minor isomer). A small downfield shift of 2.0 ppm is observed for $\delta^{13}C$ of the methylene groups (Figure 2).

The coupling constants between ^{31}P and ^{15}N are nearly identical (about 90 Hz) for the minor and the major isomer. This is in good agreement with the values reported in the literature for a similar compound incorporating benzene-1,2-diol as the chelating unit and the *N*, *N*-dimethylamine moiety bonded to phosphorus.[28] The bonding of nitrogen to the trivalent phosphorus atom causes a marked shift of the ^{15}N NMR signal to lower field as compared to the ^{15}N resonance of neat *N*, *N*-diethylamine. This shift amounts to 46 ppm for the main isomer and 43 ppm for the minor isomer (Figure 3). As in the case of **1**, the ring protons in **2** display the ABM-part of an $[ABM]_2X$ spectrum.

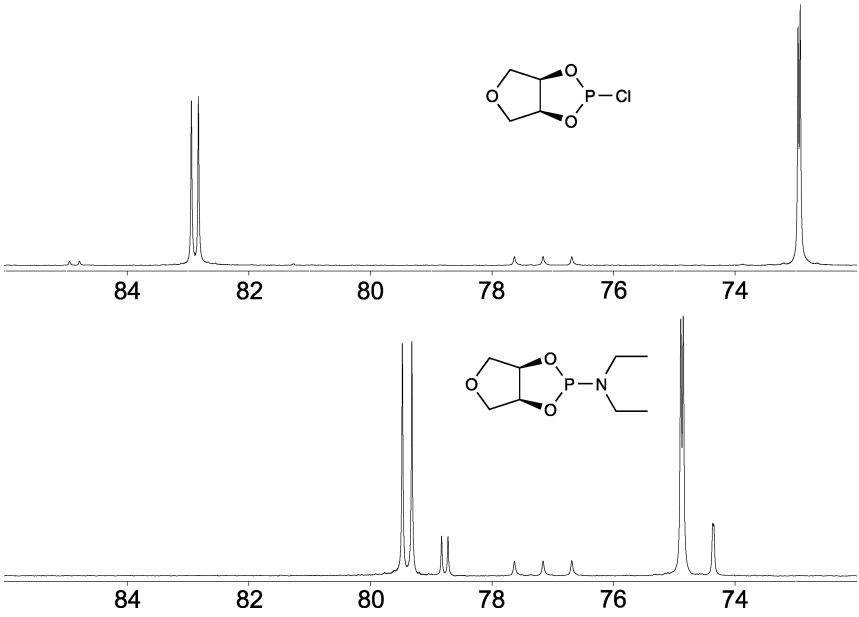


FIGURE 2 ^{13}C NMR spectra of 2-chloro-tetrahydro-furo[3,4-*d*][1,3,2]dioxaphosphole (**1**) (top) and diethyl-(tetrahydro-furo[3,4-*d*][1,3,2]dioxaphosphol-2-yl)-amine (**2**) (bottom) recorded in $CDCl_3$. For clarity, only the region containing the resonances attributable to the anhydroerythritol moiety is shown.

Reaction of **2** with one equivalent of anhydroerythritol and subsequent removal of the liberated *N*, *N*-diethylamine by distillation yielded a colorless crystalline solid. The same product was also obtained in a one-step procedure after prolonged heating of tris(*N*,*N*-dimethylamino)phosphane with two equivalents of anhydroerythritol in toluene.

The $^{31}P\{^1H\}$ NMR spectrum of the dissolved crystalline product shows three resonances around −20 ppm. The values are in the range that was reported in the literature for hydrido-spiro-λ^5-phosphanes resulting from vicinal diols and provide a first indication for the formation of **3**.[10–12] The intensity of the two signals at −20 and −22 ppm is significantly larger than that of the third resonance at −18 ppm with a relative signal ratio of 1:5:4 (from lowest to highest field). As in the case of **2**, the appearance of three distinct resonances is indicative of *syn*/*anti* isomerism which is caused by the possible orientations of the *meso*-oxolan rings with respect to the hydrogen atom at phosphorus. In the proton coupled ^{31}P NMR spectrum the signals split into dubletts with a large P,H coupling constant and further into different multiplets with much

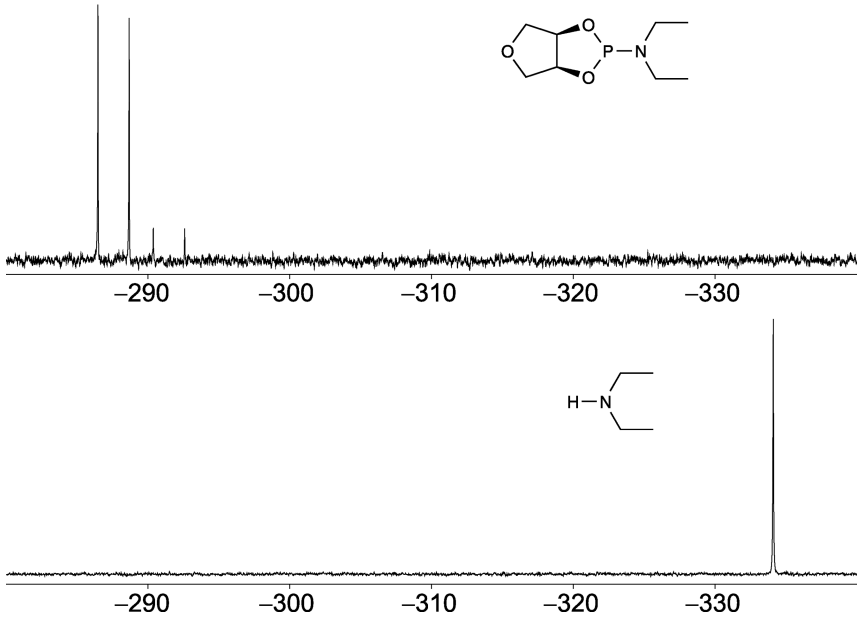


FIGURE 3 ^{15}N NMR spectra of diethyl-(tetrahydro-furo[3,4-*d*][1,3,2] dioxaphosphol-2-yl)-amine (**2**) (top) and *N*, *N*-diethylamine (bottom) as neat samples. The presence of two isomers as well as the ^{31}P-^{15}N-coupling and the marked downfield shift of the nitrogen resonance in **2** relative to the pure amine are clearly visible.

smaller P,H coupling constants. The large P,H coupling constants range between 820 and 830 Hz, which is typical for compounds of pentacoordinated phosphorus with direct P-H bonds, thus further corroborating the identity of **3**.[10–12] The proton coupled ^{31}P NMR spectrum allows for the identification of the *syn*/*syn*-, the *syn*/*anti*- and the *anti*/*anti*-isomer on the basis of the splitting patterns and the signal intensities. The signal at −22 ppm with the most complex splitting pattern is caused by the *syn*/*anti* isomer due to the C_2 symmetry of this molecule, which makes the hydrogen atoms at the CH-moieties unequal. For the identification of the other two isomers, the splitting pattern no longer can be used as the only discriminating tool due to the C_s symmetry of these two stereoisomers. It is the marked difference in signal intensities, which allows for a tentative assignment of the resonances. DFT calculations at the B3LYP/aug-CCpVDZ level of theory with Gaussian03[29] for both isomers show the *anti*/*anti* isomer to be 10.6 kJ mol^{-1} more unfavorable than the *syn*/*syn* isomer. Thus the resonance with the higher intensity at −20 ppm may be attributed to *syn*/*syn* isomer.

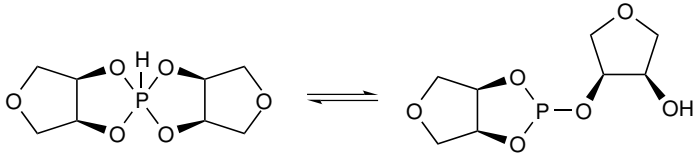


FIGURE 4 Equilibrium between the (formal) P^{V} (left) and the P^{III} (right) isomer of **3**.

The ^{13}C NMR spectrum of **3** further supports the proposed structure. Assignment of the signals is based on a ^{13}C DEPT-90 experiment. The number of signals for the methine and methylene moieties observed is in accord with the presence of the three stereoisomers discussed.

The IR spectrum of **3** shows the absence of free hydroxyl groups thus ruling out the possibilty of **3** being a λ^3-phosphane. At the same time the absorption at 2439 cm^{-1} in the infrared spectrum and the emission at 2437 cm^{-1} in the Raman spectrum, prove the presence of a P-H bond.[30]

A small melting range of only around 2.5°C is observed for **3** even at a heating rate of only 1°C per min with resolidification occurring almost instantaneously upon removal from the heating source. Obviously, an adjustment of the equilibrium between P^{III} and (formal) P^{V} (Figure 4) either does not take place or it proceeds so quickly, that no broad hysteresis can be observed for melting or resolidification, as was described for the ethylene glycol derived hydrido-spirophosphorane.[31]

Unfortunately, despite of several attempts of recrystallization, the poor quality of the crystals obtained from **3** precluded the determination of its molecular structure by means of single crystal X-ray diffraction.

Compound **3** is not stable against prolonged exposure to air or moisture neither in solid state nor in solution. It easily decomposes with cleavage of the P–H and the P–O bonds, yielding – predominantly – phosphates.

CONCLUSION

Using anhydroerythritol as vicinal diol and starting from phosphorus trichloride a new compound containing a pentacoordinate phosphorus atom was synthesized in three steps. Its NMR, IR and Raman data unambiguously identify the compound as a symmetric hydrido-spiro-λ^5-phosphane. The synthetic protocols reported in the literature for the synthesis of hydrido-spiro-λ^5-phosphanes with open-chain diols were thus successfully applied to the synthesis of a cyclopentane-derived diol.

The anhydroerythritol was used in this study as a configurationally stable, non-reducing model compound for important sugars like D-ribose. The formation of the hydrido-spiro-λ^5-phosphane **3** indicates, that a an analogous synthetic route might be applied for the preparation of hydrido-spiro-λ^5-phosphanes derived from carbohydrates as chelating dioles. The synthesis of symmetric carbohydrate-substituted spiro-λ^5-phosphanes having a sterically non-demanding hydrogen atom as the fifth substituent is of great importance. Such compounds would provide precious information not only about the structures of postulated hypervalent phosphorus containing intermediates in metabolism, but also in the field of asymmetric catalysis, where diol-derived hydrido-spiro-λ^5-phosphanes have already been applied as interesting ligands for transition metal complexes.[32,33]

EXPERIMENTAL

Phosphorus trichloride (synthesis grade) was obtained from Merck and used without further purification. Anhydroerythritol was synthesized according to a published procedure.[34] *meso*-Erythritol was obatined from Acros and used as received. Resinous ion exchanger Amberlite IR-120 was obtained from Aldrich in protonated form and applied without further purification. Toluene, benzene and dichloromethane (all Fluka) were dried over molecular sieves (4 Å) prior to use. *N*,*N*-Diethylamine (synthesis grade, Fluka) was stored over potassium hydroxide pellets for several days before use. Tris(dimethylamino)phosphane (Fluka) was used as received. All manipulations were carried out in flame-dried glass-ware under an atmosphere of dry nitrogen applying standard Schlenk-techniques.

^{1}H NMR spectra were measured on a JEOL Eclipse spectrometer at 270 MHz and are referenced to internal tetramethylsilane or the respective solvent residual peak.[35] ^{13}C NMR spectra were obtained with a JEOL Eclipse spectrometer at 68 MHz and are referenced to internal tetramethylsilane or the respective solvent residual peak.[35] ^{14}N and ^{15}N NMR spectra were measured on a JEOL Eclipse spectrometer at 29 MHz and 41 MHz, respectively, and are referenced to external nitromethane. ^{31}P NMR spectra were obtained with a JEOL Eclipse spectrometer at 109 MHz and are referenced to external 85% H_3PO_4. Downfield shifts are indicated by positive values. Unless otherwise stated all signals were detected as singulets. IR spectra were recorded with a Perkin Elmer Spectrum BX FT-IR spectrometer with a DuraSamplIR II ATR unit and a Bruker IFS 66v/S FTIR spectrometer. Raman spectra were measured with a Perkin Elmer 2000

NIR-FT spectrometer. UV/VIS spectra were measured with a CARY 50 Bio UV-Visible spectrometer in quartz glass cuvettes; extinction coefficients were not determined. Elemental analyses were performed with a Vario Elementar EL apparatus. Determination of the chlorine content was done according to the procedure of *Schöniger* with the help of a Metrohm Titroprocessor.[36,37] The phosphorus content was determined by ICP-AES on a Varian-VISTA Simultan spectrometer. Melting points were obtained on a Büchi-540 apparatus and are uncorrected. Refractory indices were measured on a Schmidt-Haensch DUR W2 apparatus at 25°C; thermostatization was achieved by means of a Haake B5 waterbath operated with a Haake F6 control device. Single crystal X-ray studies were performed on a Nonius Kappa CCD diffractometer.

Due to the sometimes scarce information in the literature, detailed experimental information is given also for the literature procedures followed.

Synthesis of Anhydroerythritol

In a round-bottomed flask (250 mL), equipped with a Vigreux-column-equipped distillation head, *meso*-erythritol (50.00 g, 409 mmol) and Amberlite IR-120 (5.04 g) were thoroughly mixed by shaking. The mixture was then molten by means of an electrical heating device and the obtained crude product continuously removed from the reaction vessel by distillation (3.5 mbar, 113°C at the top of the distillation head). For drying, the crude product was dissolved in dichloromethane (150 mL), and the colorless solution was stored over molecular sieves (35 g, 4 Å) for three days. After filtration the solvent was removed under reduced pressure and the residue was once again distilled (identical conditions as given above). A colorless and odorless viscous liquid was obtained, which solidified upon storage at 4°C. Yield: 31.29 g, 301 mmol, 73.6%. ρ = 1.38 g·cm^{-3}. ^{1}H NMR (DMSO-d$_6$, 270.2 MHz, 24°C): δ = 4.71 (d, *J*= 3.8 Hz, 2H, OH), 4.04–3.96 (m, 2H, C*H*OH), 3.76–3.71 (m, 2H, CH_2O), 3.47–3.42 (m, 2H, CH_2O). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 67.9 MHz, 26°C): δ = 72.1 (CH_2O), 70.9 (CHOH). Elemental analysis: Found (calculated for $C_4H_8O_3$): C 45.99% (46.15%), H 7.89% (7.75%). MS (DEI$^+$) *m/z* (rel. intensity): 105 (48, [M + H]$^+$), 104 (13, [M]$^+$), 87 (43, [M−OH]$^+$), 70 (0.4, [M−OH−OH]$^+$). IR (KBr): ν = 3381 (s), 2949 (s), 2877 (s), 1466 (m), 1416 (m), 1364 (m), 1335 (m), 1213 (m), 1128 (s), 1058 (s), 992 (m), 904 (m), 874 (m), 736 (w), 661 (w), 558 (w), 418 (w) cm^{-1}. Raman (neat): ν = 3363 (22), 2954 (100), 2880 (81), 1478 (51), 1294 (28), 1215 (37),

1125 (29), 989 (26), 907 (54), 859 (89), 735 (22), 562 (43), 388 (32) cm^{-1}. Refractory index: 1.4733.

Synthesis of 2-Chloro-tetrahydro-furo[3,4-*d*][1,3,2] dioxaphosphole (1)

In a three-necked flask (250 mL), equipped with a dropping funnel and a pressure equalizing valve, phosphorus trichloride (8.75 mL, 13.73 g, 100 mmol) was dissolved in dichloromethane (50 mL). With vigorous stirring a solution of anhydroerythritol (7.54 mL, 10.41 g, 100 mmol) in dichloromethane (10 mL) was dropped to this mixture in the course of 30 min; during this time a strong evolution of gaseous reaction products was observed. After completion of the addition, the reaction mixture was stirred for 4 h at room temperature and then for additional 30 min at approximately 40°C (waterbath). All volatile components from the reaction mixture were removed at room temperature under reduced pressure. The residue was distilled under reduced pressure over a Vigreux column (2.0×10^{-2} mbar, 59°C at the top of the distillation head). A colorless, slightly oily liquid with a pungent garlic-like odor was obtained, which solidified after storage for several weeks at room temperature to give a colorless crystalline solid with a pungent odor. Both liquid and solid samples fumed upon exposal to air. Yield 13.43 g, 79.7 mmol, 79.7%. $\rho = 1.44\ g\,cm^{-3}$ (as liquid sample). ^1H NMR ($CDCl_3$, 270.2 MHz, 25°C): $\delta = 5.22$–5.17 (m, 2H, HCO), 4.13–4.08 (m, 2H, CH_2), 3.60–3.50 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.9 MHz, 26°C): $\delta = 84.9$ (d, J_{PC}= 11.2 Hz, HCO, minor isomer), 82.9 (d, $J_{PC} = 8.0$ Hz, HCO, major isomer), 72.9 (d, $J_{PC} = 2.3$ Hz, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 109.4 MHz, 25°C): $\delta = 183$ (minor isomer), 175 (major isomer). Elemental analysis: Found (calculated for $C_4H_6ClO_3P$): C 28.61% (28.51%) H 3.64% (3.59%), Cl 16.41% (21.04%); ICP-AES: Found (calculated for $C_4H_6ClO_3P$): P 17.15% (18.38%); the larger deviations in the case of chlorine and phosphorus are due to problems while preparing the highly moisture sensitive compound for analysis. MS (EI^+) *m/z* (rel. intensity): 168 (0.7, $[M]^+$), 133 (39, $[M-Cl]^+$), 69 (100, $[M-PO_2Cl-H]^+$). IR (KBr): $\nu = 2993$ (w), 2923 (w), 2902 (w), 2861 (w), 2725 (w), 1784 (w), 1750 (w), 1461 (w), 1448 (w), 1337 (m), 1309 (m), 1266 (m), 1230 (w), 1201 (w), 1092 (s), 1049 (m), 1028 (m), 1012 (s), 979 (m), 938 (s), 917 (s), 876 (s), 849 (m), 834 (m), 816 (m), 787 (m), 765 (m), 735 (w), 714 (m), 616 (w), 590 (m), 575 (w), 550 (w), 467 (m), 412 (m) cm^{-1}. Raman (neat): $\nu = 2998$ (100), 2980 (87), 2925 (25), 2904 (21), 2868 (64), 1463 (22), 1449 (25), 1369 (8), 1342 (7), 1323 (10), 1317 (11), 1289 (10), 1266 (15), 1229 (13), 1202 (16), 1097 (18), 1084 (11), 1049 (8), 1026 (6), 1011 (24), 935 (38), 914 (13), 873

(10), 835 (7), 787 (53), 715 (40), 590 (22), 567 (23), 471 (23), 460 (60), 410 (48), 393 (19), 328 (39), 230 (19), 209 (31) cm^{-1}. UV/VIS (acetonitrile): λ_{max} = 259.1, 265.1, 272.0 nm. UV/VIS (cyclohexane): λ_{max} = 260.0, 265.5, 272.4 nm. M.p.: 44.6–46.0°C.

Synthesis of Diethyl-(tetrahydro-furo[3,4-*d*][1,3,2] dioxaphosphol-2-yl)-amine (2)

In a three-necked flask (500 mL), equipped with a dropping funnel and a pressure equalizing valve, 2-chloro-tetrahydro-furo[3,4-*d*][1,3,2]dioxaphosphole (7.61 mL, 10.95 g, 65 mmol) was dissolved in benzene (150 mL). Under cooling with an ice-bath, a solution of diethylamine (13.46 mL, 9.51 g, 130 mmol) in benzene (20 mL) was added dropwise to this solution over 30 min. Slowly, a colorless solid started to precipitate from the reaction mixture. After completion of the addition, the ice-bath was removed and the colorless suspension was stirred at room temperature overnight. The opalescing solid was removed by filtration over a coarse-sintered glas disk and from the filtrate all volatile compounds were removed under reduced pressure. The residue was distilled under reduced pressure over a Vigreux-column (2.0×10^{-2} mbar, 78°C at the top of the distillation head). A colorless, oily liquid with a garlic-like odor was obtained. Yield: 12.36 g, 60.2 mmol, 92.6%. ρ = 1.16 g cm^{-3}. ^{1}H NMR ($CDCl_3$, 270.2 MHz, 23°C): δ = 4.87–4.84 (m, 2H, HCO, major isomer), 4.64–4.59 (m, 2H, HCO, minor isomer), 4.07–4.02 (m, 2H, CH_2, minor isomer), 3.88–3.84 (m, 2H, CH_2, major isomer), 3.49–3.48 (m, 2H, CH_2, minor isomer), 3.46–3.39 (m, 2H, CH_2, major isomer), 3.11–2.99 (m, 4H, N(CH_2), minor isomer), 2.97–2.84 (m, 4H, N(CH_2), major isomer), 1.03–0.96 (m, (6+6)H, CH_3, major and minor isomer). ^{13}C{^{1}H} NMR ($CDCl_3$, 67.9 MHz, 25°C): δ = 79.4 (d, J_{PC} = 10.6 Hz, HCO, major isomer), 78.8 (d, J_{PC}= 7.3 Hz, HCO, minor isomer), 74.9 (d, J_{PC} = 2.6 Hz, CH_2, major isomer), 74.4 (d, J_{PC} = 1.3 Hz, CH_2, minor isomer), 37.9 (d, J_{PC} = 20.5 Hz, N(CH_2), major isomer), 36.6 (d, J_{PC} = 22.1 Hz, N(CH_2), minor isomer), 15.1 (d, J_{PC} = 2.9 Hz, CH_3, major and minor isomer). ^{14}N{^{1}H} NMR (neat, 28.9 MHz, 24°C): no distinct resonances visible. ^{15}N{^{1}H} NMR (neat, 40.5 MHz, 22°C): δ = −287.6 (d, J_{PN}= 89.3 Hz, major isomer), −291.5 (d, J_{PN} = 89.8 Hz, minor isomer). ^{31}P{^{1}H} NMR ($CDCl_3$, 109.4 MHz, 25°C): δ = 163 (13%), 152 (87%). Elemental analysis: Found (calculated for $C_8H_{16}NO_3P$): C 46.43% (46.83%), H 7.97% (7.86%), N 7.03% (6.83%). ICP-AES: Found (calculated for $C_8H_{16}NO_3P$): P 13.98% (15.10%). MS (DEI$^+$) *m/z* (rel. intensity): 205 (16, [M]$^+$), 190 (36, [M−CH_3]$^+$), 133 (100, [M−N(CH_2CH_3)$_2$]$^+$), 72 (26, [M−P($C_4H_6O_3$)]$^+$). IR (neat): ν = 2969 (m), 2934 (m), 2852 (m), 1461 (w), 1376 (m), 1364 (w), 1344 (w), 1322 (w), 1290 (w), 1264 (w), 1227

(w), 1204 (m), 1182 (m), 1100 (s), 1060 (m), 1036 (m), 1013 (s), 930 (s), 908 (s), 878 (w), 847 (s), 787 (m), 756 (m), 707 (w), 683 (m), 666 (m) cm^{-1}. Raman (neat): ν = 2990 (60), 2934 (100), 2870 (59), 1451 (51), 1101 (19), 1078 (28), 1041 (21), 1016 (16), 932 (35), 853 (29), 760 (30), 709 (38), 668 (69), 560 (17), 325 (25) cm^{-1}. UV/VIS (acetonitrile): λ_{max} = 204.9 nm. UV/VIS (cyclohexane): λ_{max} = 209.0 nm. Refractory index: 1.4821.

Synthesis of Hydrido-bis(*meso*-oxolanylen-3,4-dioxy) -λ^5-phosphane (3)

Method A

A mixture of diethyl-(tetrahydro-furo[3,4-*d*][1,3,2]dioxaphosphol-2-yl)-amine (8.84 mL, 10.26 g, 50.0 mmol) and anhydroerythritol (3.78 mL, 5.21 g, 50.0 mmol) was placed in a Schlenk-flask (50 mL) equipped with a distillation head. The reaction mixture was heated under a weak steady stream of nitrogen until no more liquid distilled. During the heating period, a growing amount of colorless solid formed in the Schlenk-flask, which finally completely replaced the liquid phase. Yield: 11.18 g, 47.3 mmol, 94.6%.

Method B

A solution of tris(*N*,*N*-dimethylamino)phosphane (3.64 mL, 3.26 g, 20 mmol) in toluene (10 mL) was mixed with anhydroerythritol (3.02 mL, 4.16 g, 40 mmol) in a Schlenk-flask and heated under reflux for 6 h. A steady stream of nitrogen was passed through a pressure equalizing valve located at the head of the reflux condenser throughout the heating period. Upon cooling to room temperature, a white crystalline solid was obtained from the colorless reaction mixture. Removal of the solvent under reduced pressure afforded a white crystalline solid. Yield: 1.42 g, 6.01 mmol, 30.1%.

^{1}H NMR ($CDCl_3$, 270.2 MHz, 22°C): δ = 7.26 (d, J_{PH} = 832 Hz, 1H, PH, minor isomer, *syn* or *anti*), 7.15 (d, J_{PH} = 831 Hz, 1H, PH, *syn*/*anti*), 7.13 (d, J_{PH} = 822 Hz, 1H, PH, *syn* or *anti*), 4.64–4.53 (m, HCO), 4.09–3.88 (m, CH_2), 3.50–3.41 (m, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.9 MHz, 25°C): δ = 75.5 (d, J_{PC}= 1.8 Hz, CH), 74.70 (d, J_{PC} = 3.2 Hz, CH_2), 74.66 (CH_2), 74.5 (CH), 74.3 (d, J_{PC} = 2.1 Hz, CH_2), 74.2 (d, J_{PC} = 1.2 Hz, CH_2), 74.1 (d, J_{PC} = 1.2 Hz, CH), 73.8 (CH). ^{31}P NMR ($CDCl_3$, 109.4 MHz, 25°C): δ = −18 (dq, $^1J_{PH}$= 833 Hz, $^3J_{PH}$= 16.4 Hz, *syn* or *anti*, 11%), −20 (dq, $^1J_{PH}$= 822 Hz, $^3J_{PH}$= 12.0 Hz, *syn* or *anti*, 47%), −22 (dm, $^1J_{PH}$= 832 Hz, *syn*/*anti*, 42%). Elemental analysis: Found (calculated for $C_8H_{13}O_6P$): C 40.65% (40.69%), H 6.26% (5.55%). ICP-AES: Found (calculated for $C_8H_{13}O_6P$): P 12.48% (13.12%); the large

deviation in the case of phosphorus is due to problems while preparing the highly moisture-sensitive compound for analysis. MS (DCI^+, isobutane) *m/z*: 237 ($[M+H]^+$), 151 ($[M-C_4H_6O_2+H]^+$). IR (neat): ν = 2988 (w), 2940 (m), 2901 (w), 2844 (m), 2725 (w), 2675 (w), 2647 (w), 2439 (w), 1463 (w), 1448 (w), 1374 (w), 1352 (w), 1336 (w), 1286 (w), 1263 (w), 1233 (w), 1204 (w), 1103 (s), 1060 (m), 1032 (s), 996 (w), 947 (m), 906 (s), 891 (s), 845 (s), 782 (m), 728 (s), 711 (s), 652 (m), 631 (m), 584 (w) cm^{-1}. Raman (neat): ν = 2995 (100), 2981 (43), 2942 (67), 2906 (38), 2845 (44), 2437 (32), 1462 (37), 1337 (14), 1264 (17), 1205 (13), 1106 (16), 1057 (22), 945 (31), 913 (38), 869 (22), 817 (8), 757 (41), 730 (48), 588 (17), 526 (25), 481 (12), 336 (25), 183 (18) cm^{-1}. M.p.: 110.9–113.5°C.

Crystal Structure Determination and Refinement

A single crystal suitable for X-ray diffraction was selected by means of a polarizing microscope and mounted on the tip of a glass fiber. Data collection was performed on a Nonius Kappa CCD diffractometer using graphite-monochromatized MoKα radiation (λ= 0.71073 Å). The structure was solved by Direct Methods (SIR 97[38]) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97[39]). Anisotropic displacement parameters were refined for all non-hydrogen atoms. Correct assignment of space group and search for missed or additional symmetry was performed with PLATON to check whether an orthorhombic setting was chosen correctly over a tetragonal one despite the nearly identical lengths of axes *b* and *c*.[40] Molecular graphics were drawn with ORTEPIII.[41]

Crystallographic Data for 1

$C_4H_6ClO_3P$, M_r = 168.51 g mol^{-1}, colorless platelet, 0.21 × 0.17 × 0.04 mm, orthorhombic, *Pbca*, *a* = 9.5680(2), *b* = 11.8940(3), *c* = 11.8950(2) Å, V = 1353.67(5) $Å^3$, Z = 8, ρ = 1.654 g·cm^{-3}, T = 200(2) K, μ(MoKα) = 0.730 mm^{-1}, multi-scan absorption correction, θ range: 3.22–27.46°, 2853 refls., 1543 independent and used in refinement, 1322 with $I \geq 2\sigma(I)$, R_{int} = 0.0118, mean $\sigma(I)/I$ = 0.0156, 83 parameters, $R(F_{obs})$ = 0.0303, $R_w(F^2)$ = 0.0827, S = 1.069, min. and max. residual electron density: −0.430/0.332 e $Å^{-3}$, max. shift/error = 0.001.

Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre (**1**: 655562). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336–033; e-mail for inquiry: file-server@ccdc.cam.ac.uk).

REFERENCES

[1] L. Stryer, *Biochemistry*, (W. H. Freeman and Co., New York, 1988), 3rd ed.
[2] F. H. Westheimer, *Acc. Chem. Res.*, **1,** 70 (1968).
[3] J. A. Gerlt, F. H. Westheimer, and J. M. Sturtevant, *J. Biol. Chem.*, **250,** 5059 (1975).
[4] R. R. Holmes, *Acc. Chem. Res.*, **31,** 535 (1998).
[5] R. R. Holmes, *Acc. Chem. Res.*, **37,** 746 (2004).
[6] S. D. Lahiri, G. Zhang, D. Dunaway-Mariano, and K. N. Allen, *Science*, **299,** 2067 (2003).
[7] N. V. Timosheva, A. Chandrasekaran, and R. R. Holmes, *J. Am. Chem. Soc.*, **127,** 12474 (2005).
[8] N. V. Timosheva, A. Chandrasekaran, and R. R. Holmes, *Inorg. Chem.*, **45,** 3113 (2006).
[9] N. V. Timosheva, A. Chandrasekaran, and R. R. Holmes, *Inorg. Chem.*, **45,** 10836 (2006).
[10] A. Munoz, M. Sanchez, M. Koenig, and R. Wolf, *Bull. Soc. Chim. France*, 2193 (1974).
[11] R. Burgada, *Bull. Soc. Chim. France*, 407 (1975).
[12] M. Sanchez, R. Wolf, R. Burgada, and F. Mathis, *Bull. Soc. Chim. France*, 773 (1967).
[13] H. Germa, M. Sanchez, R. Burgada, and R. Wolf, *Bull. Soc. Chim. France*, 612 (1970).
[14] H. Wunderlich and H.-G. Wussow, *Acta Cryst. B*, **34,** 2663 (1978).
[15] V. F. Zheltukhin, A. I. Dovbysh, D. N. Sadkova, A. B. Dobrynin, O. N. Kataeva, I. A. Litvinov, and V. A. Alfonsov, *Russ. Chem. Bull.*, **54,** 1935 (2005).
[16] R. Burgada, *Ann. Chim.*, **8,** 347 (1963).
[17] Z. Fei, A. M. Z. Slawin, and J. D. Woollins, *Polyhedron*, **20,** 3355 (2001).
[18] P. G. Jones, C. Kunze, H. Thönnessen, and R. Schmutzler, *Acta Crystallogr., Sect. E*, **58,** o1432 (2002).
[19] P. G. Jones, C. Kunze, M. Freytag, and R. Schmutzler, *Acta Crystallogr., Sect. E*, **58,** o1434 (2002).
[20] A. Chandrasekaran, R. O. Day, P. Sood, N. V. Timosheva, D. J. Sherlock, and R. R. Holmes, *Phosphorus, Sulfur and Silicon*, **160,** 1 (2000).
[21] M. Cattani-Lorente, M. Geoffroy, S. P. Mishra, J. Weber, and G. Bernardinelli, *J. Am. Chem. Soc.*, **108,** 7148 (1986).
[22] D. J. Sherlock, A. Chandrasekaran, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **36,** 5082 (1997).
[23] A. Vollbrecht, I. Neda, H. Thönnessen, P. G. Jones, R. K. Harris, L. A. Crowe, and R. Schmutzler, *Chem. Ber.*, **130,** 1715 (1997).
[24] P. Sood, M. Koutha, M. Fan, Y. Klichko, H. Zhang, and M. Lattman, *Inorg. Chem.*, **43,** 2975 (2004).
[25] T. Kop-Weiershausen, J. Lex, J.-M. Neudörfl, and B. Goldfuss, *Beilstein J. Org Chem.*, **1,** no pp given (2005).
[26] D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, **97,** 1354 (1975).
[27] J. C. Tebby, *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data* (CRC Press, Boca Raton, 1991).
[28] G. A. Gray and T. A. Albright, *J. Am. Chem. Soc.*, **99,** 3243 (1977).
[29] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y.

Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03, Revision B.03/D.01.,* Gaussian, Inc., Wallingford CT, **2004**.

[30] J. Weidlein, U. Müller, and K. Dehnicke, *Schwingungsfrequenzen I* (Thieme, Stuttgart, 1981).

[31] N. P. Grechkin, R. R. Shagidullin, and G. S. Gubanova, *Bull. Acad. Sci. USSR Chem. Sci.*, **8,** 1700 (1968); original: *Izvestiya Akad. Nauk SSSR, Ser. Khim.*, **8,** 1797 (1968).

[32] W. K. Rybak, A. Skarzynska, and T. Glowiak, *Angew. Chem. Int. Edt.*, **42,** 1725 (2003); *Angew. Chem.*, **115,** 1767 (2003).

[33] W. K. Rybak, A. Skarzynska, L. Szeterenberg, Z. Ciunik, and T. Glowiak, *Eur. J. Inorg. Chem*., **24,** 4964 (2005).

[34] F. H. Otey and C. L. Mehltretter, *J. Org. Chem.*, **26,** 1673 (1961).

[35] H. E. Gottlieb, V. Kotlyar, and A. Nudelman, *J. Org. Chem.*, **62,** 7512 (1997).

[36] W. Schöniger, *Mikrochim. Acta*, **43,** 123 (1955).

[37] W. Schöniger, *Mikrochim. Acta*, **44,** 869 (1956).

[38] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, *J. Appl. Crystallogr.*, **32,** 115 (1999).

[39] G. M. Sheldrick, *SHELXL97* (University of Göttingen, Germany, 1997).

[40] A. L. Spek, *PLATON—A Multipurpose Crystallographic Tool* (Utrecht University, Utrecht, the Netherlands, 2005).

[41] M. N. Burnett and C. K. Johnson, *ORTEPIII* (Oak Ridge National Laboratory, Tennessee, USA, 1996), Report ORNL-6895.