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Synthesis of chiral phosphazene bases

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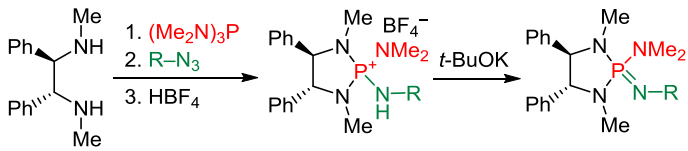


Air-stable and crystalline tetraaminophosphonium tetrafluoroborates possessing chiral, enantiomerically pure 1,2-diamine moiety have been synthesized by a three-step sequential one-pot approach. The tetrafluoroborate salts can be purified by recrystallization or chromatography and subsequently converted to the phosphazene bases by treatment with *t*-BuOK. Basicity values in tetrahydrofuran have been measured for the obtained phosphazene bases by means of spectrophotometric titration.

Keywords: phosphazene bases, tetraaminophosphonium salts, basicity, one-pot synthesis, pK_{ip} value.

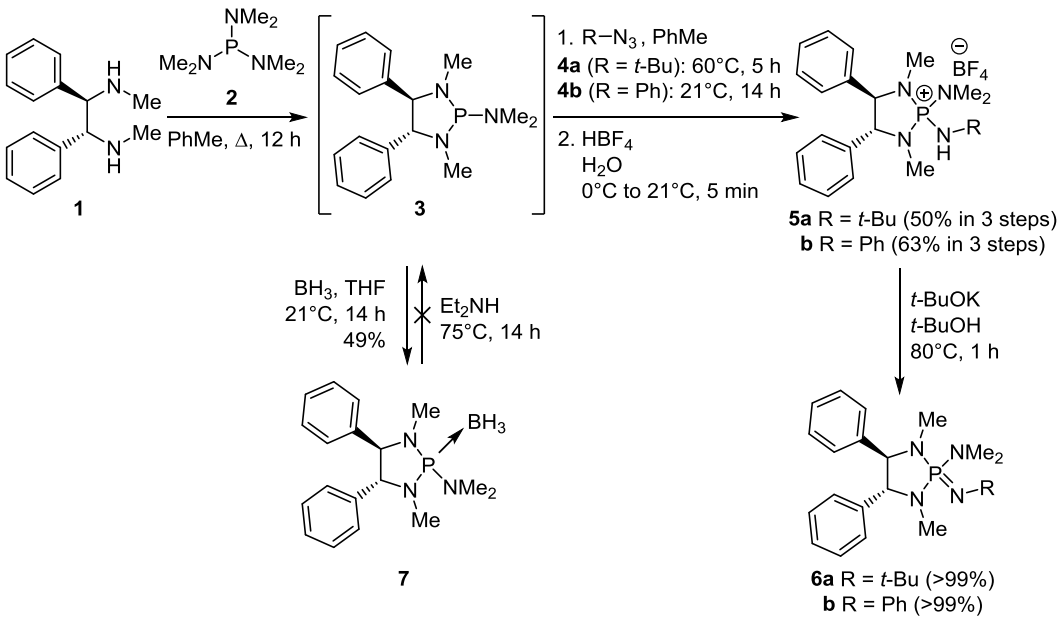
Phosphazene bases (PBs) have been widely employed in stoichiometric amounts as strong non-nucleophilic bases in a range of organic transformations,[1] including stereoselective transformations, such as: Mukaiyama aldol reaction, asymmetric alkylation, Henry reaction, and Julia–Kocienski olefination.[1b,2] However, information regarding the use of chiral PBs to catalyze enantioselective reactions is rather scarce.[3] Thus, chiral PBs have been used as ligands in a copper-catalyzed enantioselective cyclopropanation reaction[3a] and also as catalysts in enantioselective amination of 2-alkyltetralone derivatives and their analogs.[3b] Ooi has successfully utilized chiral PBs in stereoselective hydrophosphonylation of aldehydes,[3c] Michael addition,[3d] and Payne-type oxidation of *N*-sulfonyl imines.[3e]

There are a number of synthetic methods for the preparation of PBs.[1b,3,4,5] Among them, Alexandrova et al. demonstrated a synthesis of PBs by the Staudinger reaction between triaminophosphanes and alkyl azides.[4c] The advantages of this approach are readily available starting materials, simple product isolation procedure, and good yields. Therefore we decided to adapt this methodology for the synthesis of new PBs with backbone chirality. In the meantime, we were also aware of difficulties with purification of PBs. Thus, most of the known PBs are oil-like materials and relatively high basicity of PBs complicates their purification by chromatographic methods. Furthermore, distillation under high vacuum, a commonly used method for the purification of PBs, apparently is not suitable for the small-scale synthesis of higher molecular weight PBs possessing structurally complex chiral moieties. Herein, we report that chiral 1,2-diphenyl diamine-based PBs can be conveniently purified by preparation of the corresponding tetrafluoroborate salts. Previously unreported PBs with chiral backbone have been obtained in a multistep sequential one-pot synthesis from chiral, enantiomerically pure 1,2-diamine.

The synthesis of chiral PBs commenced with the preparation of triaminophosphane **3** from hexamethylphosphorous triamide (**2**) and the chiral 1,2-diamine **1** (Scheme 1). Incomplete conversion of the chiral 1,2-diamine **1** (93%) after prolonged heating (>12 h) was accompanied by concomitant decomposition of the reaction product **3** (^{31}P NMR assay). The triaminophosphane **3** was also found to be unstable in air, as well as in the presence of moisture and protic solvents. The poor stability of the non-crystalline phosphane **3** complicated its isolation and separation from the unreacted starting materials **1** and **2**, so we looked for other approaches, such as *in situ* derivatization to obtain a stable, crystalline, and easy-to-purify material.

Tertiary phosphine–borane complexes are relatively stable and usually appear to be crystalline. They can be easily prepared in reactions with borane and subsequently cleaved to release free phosphines.[6] We envisaged that the preparation of crystalline complex between borane and triaminophosphane **3** would allow for efficient purification of compound **3**. Indeed, the desired complex **7** was readily formed in the reaction between borane and phosphane **3**

Scheme 1



and was recrystallized from EtOAc to >95% purity (^{1}H and ^{31}P NMR). The structure of complex **7** was confirmed by X-ray crystallographic analysis (Fig. 1). With the purified triaminophosphane–borane complex **7** in hand, cleavage of the complex **7** to triaminophosphane **3** by reaction with excess of Et_2NH was attempted. The desired compound **3** was not obtained at room temperature, whereas at elevated temperatures (100°C) decomposition of the formed triaminophosphane **3** was observed by ^{31}P NMR method. Apparently, the required harsh reaction conditions for cleaving the remarkably stable Lewis acid–base complex **7**[7] were not compatible with the relatively sensitive triaminophosphane **3**. Therefore we decided to avoid the isolation and purification of intermediate **3** during the multistep synthesis of PBs **6**.

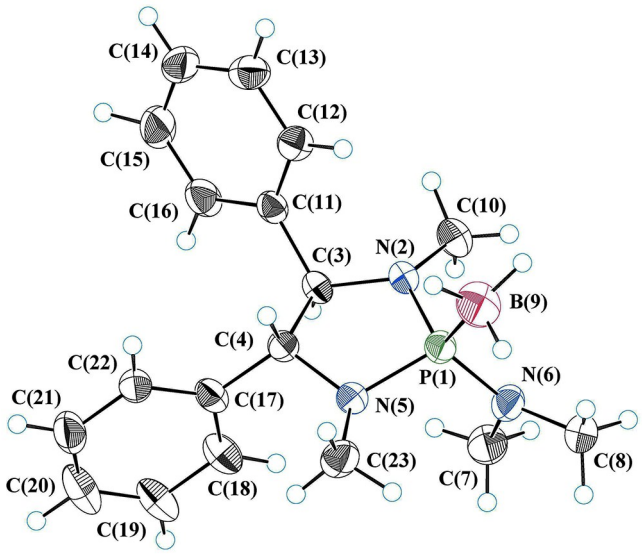
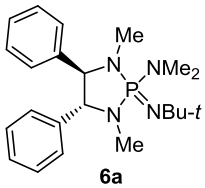
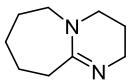
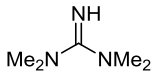
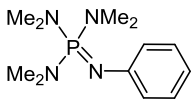
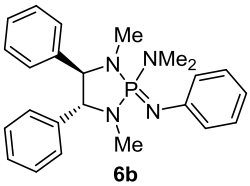


Figure 1. The molecular structure of triaminophosphane–borane complex **7** with atoms represented by thermal vibration ellipsoids of 50% probability.

Instead, the phosphane **3** was converted without isolation to the target phosphazenes **6a**,**b** in reactions with *tert*-butyl azide (**4a**) or phenyl azide (**4b**), respectively. As anticipated, both PBs **6a**,**b** turned out to be oily materials, which complicated their isolation from the reaction mixture and subsequent purification. Therefore we sought a suitable acid to form crystalline salts of PBs **6a**,**b** that could be more convenient to handle. We chose HBF_4 as the most suitable acid because tetrafluoroborate salts of several PBs have been used for the preparation of crystals for X-ray analysis.[4b,c] Hence, treatment of the reaction mixture containing phosphazenes **6a**,**b** with aqueous HBF_4 solution followed by extraction into the organic phase provided crystalline and stable tetrafluoroborates **5a**,**b** (50% and 63% yields, respectively, calculated for three steps starting from the 1,2-diamine **1**). The purity of these salts could be increased to >95% by crystallization from EtOAc or reversed-phase chromatography. The purified salts **5a**,**b** were converted back into the free bases **6a**,**b** in 99% yield by treatment with *t*-BuOK in *t*-BuOH (Scheme 1).

Basicity of the obtained chiral PBs **6a**,**b** in tetrahydrofuran was measured using UV-vis spectrophotometric titration method (Table 1, entries 1 and 6)[8] and the obtained values were compared to those of other representative organic bases. Basicity of the phosphazene **6a** was equal or higher than for DBU, 1,1,3,3-tetramethylguanidine, pyrrolidine, and PhP_1(dma) (entry 1 vs entries 2–5). Notably, the PB **6a** containing a *tert*-butylimino moiety was approximately 4 pK_{ip} units more basic than the analog **6b** containing a phenylimino group. The marked difference in basicity apparently resulted from the greater electron-donating ability of *tert*-butyl group compared to that of the phenyl group, and especially from the lack of strong resonance stabilization of the neutral base (as opposed to the protonated form) occurring *via* the benzene ring in compound **6b**. Determination of the basicity for compounds **6a**,**b** is a crucial step toward the application of these new chiral PBs in enantioselective synthesis.

Table 1. pK_{ip} values of phosphazene bases **6a**,**b** and several other representative bases in THF

Entry	Base	pK_{ip}
1	 **6a**	18.0
2		18.0[8b]
3		17.0[8b]
4		15.3[8b]
5		15.3[8b]
6	 **6b**	13.9

In summary, the synthesis of previously unreported chiral PBs possessing an enantiomerically pure 1,2-diamine moiety has been achieved. The synthesis relies on a three-step sequential one-pot preparation of air-stable and crystalline tetraaminophosphonium tetrafluoroborates, which can be purified by recrystallization or reversed-phase chromatography. Subsequent treatment of tetrafluoroborate salts with *t*-BuOK afforded the desired PBs. The triaminophosphane intermediate *en route* to chiral PBs was also isolated as a complex with borane and its structure was confirmed by X-ray crystallographic analysis. Basicity values in THF for the synthesized PBs have been determined by spectrophotometric titration method. The PB containing a *tert*-butylimino moiety had the same or higher basicity than DBU, 1,1,3,3-tetramethylguanidine, pyrrolidine, and PhP_1(dma). The applications of 1,2-diamine-derived chiral PBs will be reported elsewhere.

Experimental

IR spectrum of borane complex **7** was recorded on a Shimadzu IR Prestige-21 FT-IR spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were acquired on a Varian Inova 400 MR spectrometer (400, 101, and 162 MHz, respectively). The solvents were $CDCl_3$ (compound **3**) and CD_2Cl_2 (the rest of the compounds). ^{1}H NMR chemical shifts were reported relative to the residual solvent protons as internal standard (CD_2Cl_2: 5.32 ppm). Solvent carbon atoms served as internal standard for ^{13}C NMR spectra (CD_2Cl_2: 54.0 ppm). Triphenylphosphine oxide (27.0 ppm for ^{31}P nuclei) was used as internal standard for ^{31}P NMR spectra. Optical rotation measurements were performed on a PerkinElmer 141 polarimeter. Melting points were determined on an OptiMelt apparatus and were not corrected. All reagents and solvents were purchased from commercial suppliers and used without further purification. Toluene was distilled from P_2O_5 prior to use.

(4*R*,5*R*)-*N*,*N*,1,3-Tetramethyl-4,5-diphenyl-1,3,2-diazaphospholidin-2-amine (3). Compound **3** was synthesized according to a modified procedure reported previously.[9] Diamine **1**[10] (721 mg, 3.00 mmol) and hexamethylphosphorous triamide (**2**)[11] (0.6 ml, 3.00 mmol) were placed in a pressure vial, dissolved in anhydrous toluene (1.5 ml) under argon and heated at 110°C. After 4 h, the reaction mixture was cooled to room temperature and flushed with argon to remove the formed dimethylamine. The heating and flushing procedure was repeated 2 times (overall time of heating 12 h). The conversion of the starting material was monitored by ^{31}P NMR spectroscopy. The reaction mixture was cooled to room temperature and flushed with argon. The obtained solution of crude product **3** in toluene was diluted with anhydrous toluene to 5 ml volume and the resulting 0.6 M solution was directly used in the synthesis of PBs **6a**,**b** without further purification. ^{31}P NMR spectrum, δ, ppm: 124.2.[9]

(4*R*,5*R*)-2-*tert*-Butylamino-2-dimethylamino-1,3-dimethyl-4,5-diphenyl[1,3,2]diazaphospholidin-2-ium tetrafluoroborate (5a). A solution of *tert*-butyl azide (**4a**)[12] in toluene (1 M, 2.0 ml, 1.96 mmol) was added to the previously obtained solution of crude triaminophosphane **3** (0.6 M, 3.0 ml, 1.78 mmol) under argon. The reaction mixture was heated at 60°C for 5 h and the conversion of the starting material was monitored by ^{31}P NMR spectroscopy. After cooling to 0°C, a solution of HBF_4 in water (50% (v/v), 0.33 ml, 2.67 mmol) was added. The reaction mixture was allowed to warm up and was well stirred at room temperature for 5 min. Water (25 ml) was added and the mixture was extracted with EtOAc (2 × 25 ml). The combined organic extracts were washed with brine (25 ml), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by crystallization from EtOAc. Yield 420 mg (50%), white solid, mp 151–152°C (EtOAc). $[\alpha]_D^{20}$ 14.4 (*c* 1.00, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.52 (9H, s, $C(CH_3)_3$); 2.50 (6H, dd, *J* = 11.2, *J* = 5.0, $N(CH_3)_2$); 3.05 (6H, d, *J* = 9.7, $\underline{H}_3CNPNC\underline{H}_3$); 4.18 (2H, s, PhC$\underline{H}C\underline{H}$Ph); 4.87 (1H, d, *J* = 9.0, NH); 7.05–7.14 (4H, m, H Ar); 7.31–7.41 (6H, m, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 29.4 (d, *J* = 4); 30.9 (d, *J* = 2); 31.8 (d, *J* = 5); 38.9 (d, *J* = 4); 70.9 (d, *J* = 12); 72.7 (d, *J* = 9); 128.5 (s); 128.7 (s); 129.6 (d, *J* = 6); 129.8 (d, *J* = 13); 135.0 (d, *J* = 11); 135.2 (d, *J* = 8). ^{31}P NMR spectrum, δ, ppm: 38.0. Found, *m*/*z*: 385.2521 $[M]^+$. $C_{22}H_{34}N_4P$. Calculated, *m*/*z*: 385.2521.

(4*R*,5*R*)-2-(Dimethylamino)-1,3-dimethyl-4,5-diphenyl-2-(phenylamino)-1,3,2-diazaphospholidin-2-ium tetrafluoroborate (5b). A solution of phenyl azide (**4b**)[13] in toluene (1 M, 0.6 ml, 0.59 mmol) was added to the previously obtained solution of crude triaminophosphane **3**

(0.6 M, 0.9 ml, 0.54 mmol) under argon. The reaction mixture was stirred at 21°C for 14 h and the conversion of the starting material was monitored by ^{31}P NMR spectroscopy. After cooling to 0°C, a solution of HBF_4 in water (50% (v/v), 0.1 ml, 0.81 mmol) was added. The reaction mixture was allowed to warm up and was stirred at room temperature for 5 min. The residue was dissolved in water (15 ml) and extracted with EtOAc (2 × 25 ml). The combined organic extracts were washed with brine (25 ml), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by reversed-phase chromatography (gradient 10:100–100:0 MeCN/H_2O). Yield 168 mg (63%), white solid, mp 83–85°C (EtOAc). $[\alpha]_D^{20}$ 27.9 (*c* 1, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.49 (3H, d, *J* = 10.8, NCH_3); 2.62 (3H, d, *J* = 10.9, NCH_3); 3.13 (6H, d, *J* = 10.3, $\underline{H}_3CNPNC\underline{H}_3$); 4.02 (1H, d, *J* = 9.2, PhC<u>H</u>CHPh); 4.17 (1H, d, *J* = 9.2, PhCHC<u>H</u>Ph); 6.55–6.59 (2H, m, H Ar); 7.02–7.08 (2H, m, H Ar); 7.14–7.20 (2H, m, H Ar); 7.24–7.29 (1H, m, H Ar); 7.31–7.43 (6H, m, H Ar); 7.47–7.53 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 29.5 (d, *J* = 4); 29.7 (d, *J* = 4); 38.4 (d, *J* = 4); 71.5 (d, *J* = 12); 71.7 (d, *J* = 11); 126.5 (d, *J* = 5); 127.3 (d, *J* = 2); 128.3 (d, *J* = 8); 126.5 (d, *J* = 5); 129.4 (s); 129.6 (s); 129.7 (s); 129.9 (s); 130.5 (d, *J* = 1); 135.3 (d, *J* = 8); 135.4 (d, *J* = 9); 136.6 (d, *J* = 1). ^{31}P NMR spectrum, δ, ppm: 39.1. Found, *m*/*z*: 405.2209 $[M]^+$. $C_{24}H_{30}N_4P$. Calculated, *m*/*z*: 405.2208.

Synthesis of phosphazene bases 6a,b (General method). The appropriate PB salt **5** (0.85 mmol) was placed in a pressure vial, and a solution of *t*-BuOK in *t*-BuOH (1 M, 1.7 ml, 1.69 mmol) was added under argon. The reaction mixture was heated at 80°C for 1 h and the conversion of the starting material was monitored by ^{31}P NMR spectroscopy. After cooling to room temperature, the reaction mixture was extracted with anhydrous pentane (3 × 10 ml) and concentrated under reduced pressure.

(4*R*,5*R*)-2-(*tert*-Butylimino)-*N*,*N*,1,3-tetramethyl-4,5-diphenyl-1,3,2λ^5-diazaphospholidin-2-amine (6a). Yield 327 mg (>99%), slightly yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.32 (9H, s, $C(CH_3)_3$); 2.26 (3H, d, *J* = 9.5, NCH_3); 2.29 (3H, d, *J* = 9.6, NCH_3); 2.88 (6H, d, *J* = 9.8, $\underline{H}_3CNPNC\underline{H}_3$); 3.90 (1H, d, *J* = 9.4, PhC<u>H</u>CHPh); 3.98 (1H, d, *J* = 9.3, PhCHC<u>H</u>Ph); 7.05–7.14 (4H, m, H Ar); 7.23–7.28 (6H, m, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 30.3 (d, *J* = 4); 30.5 (d, *J* = 3); 34.5 (d, *J* = 9); 38.7 (d, *J* = 3); 71.3 (d, *J* = 10); 73.1 (d, *J* = 6); 128.6 (s); 128.7 (s); 128.7 (s); 129.1 (d, *J* = 2); 137.9 (s). ^{31}P NMR spectrum, δ, ppm: 13.5.

(4*R*,5*R*)-*N*,*N*,1,3-Tetramethyl-4,5-diphenyl-2-(phenylimino)-1,3,2λ^5-diazaphospholidin-2-amine (6b). Yield 344 mg (>99%), off-white solid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.37 (6H, dd, *J* = 9.7, *J* = 7.2, $N(CH_3)_2$); 2.98 (6H, d, *J* = 10.0, $\underline{H}_3CNPNC\underline{H}_3$); 3.99 (2H, AB, q, *J* = 14.5, PhC<u>H</u>C<u>H</u>Ph); 6.73–6.79 (1H, m, H Ar); 6.90–6.95 (2H, m, H Ar); 6.95–7.00 (2H, m, H Ar); 7.06–7.12 (2H, m, H Ar); 7.14–7.26 (5H, m, H Ar); 7.27–7.31 (3H, m, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 29.8 (d, *J* = 4); 30.5 (d, *J* = 4); 37.9 (d, *J* = 3); 72.0 (d, *J* = 10); 72.6 (d, *J* = 8); 118.2 (d, *J* = 2); 125.0 (s); 125.1 (s); 128.5 (s); 128.6 (s); 128.9 (s); 129.0 (s); 129.1 (s); 139.0 (d, *J* = 4); 139.1 (d, *J* = 5); 151.7 (d, *J* = 1). ^{31}P NMR spectrum, δ, ppm: 21.4.

(4*R*,5*R*)-*N*,*N*,1,3-Tetramethyl-4,5-diphenyl-1,3,2-diazaphospholidin-2-amine–borane complex (7). A solution of triaminophosphane **3** in dry toluene (0.6 M, 2.5 ml, 1.5 mmol) was placed in a pressure vial under argon. A solution of BH_3 in THF (1 M, 3.1 ml, 3.1 mmol) was slowly added at room temperature, and the reaction mixture was stirred for 14 h. The conversion of the starting material was monitored by ^{31}P NMR spectroscopy. Solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, gradient elution from 5% to 10% EtOAc – petroleum ether). Yield 244 mg (49%), white solid, mp 117–118°C (EtOAc). IR spectrum (KBr), ν, cm^{-1}: 2368 (BH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.25–1.11 (3H, br. m, BH_3); 2.35 (6H, ddd, *J* = 17.6, *J* = 10.9, *J* = 1.2, $N(CH_3)_2$); 2.87 (6H, dd, *J* = 9.0, *J* = 1.3, $\underline{H}_3CNPNC\underline{H}_3$); 3.82 (1H, d, *J* = 8.7, PhC<u>H</u>CHPh); 4.03 (1H, d, *J* = 8.7, PhCHC<u>H</u>Ph); 7.03–7.10 (4H, m, H Ar); 7.23–7.31 (6H, m, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 29.4 (d, *J* = 6); 31.2 (d, *J* = 10); 36.7 (d, *J* = 4); 73.3 (s); 73.7 (d, *J* = 4); 77.4 (s); 127.8 (s); 128.2 (d, *J* = 1); 128.2 (s); 128.5 (s); 128.6 (s); 138.1 (d, *J* = 5); 138.6 (d, *J* = 8). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 109.2 (dd, *J* = 204, *J* = 95). Found, %: C 65.62; H 8.36; N 12.65. $C_{18}H_{27}N_3BP$. Calculated, %: C 66.07; H 8.32; N 12.84.

X-ray structural study of compound 7. Monocrystals of compound **7**, obtained by crystallization from EtOAc ($C_{18}H_{27}BN_3P$, *M* 327.21) were orthorhombic, space group $P2_12_12_1$, at 173 K: *a* 10.1143(2), *b* 13.6442(3), *c* 13.8352(3) Å; *V* 1909.28(7) Å^3; *Z* 4; d_{calc} 1.138 g·cm^{-3}; *F*(000) 704. The intensities of 5318 reflections were determined on a Nonius Kappa CCD diffractometer (MoKα radiation, λ 0.71073 Å, 2θ < 60°), 5313 independent reflections (R_{int} 0.0076) were used in further refinement. The structure was solved directly and refined by least squares method in anisotropic full matrix approximation by F^2_{hkl}. The hydrogen atom positions were calculated geometrically and refined in isotropic approximation by the "rider" model. The final probability factor values for compound **7**: wR_2 0.135 and *GOF* 1.008 for all independent reflections (R_1 0.050 calculated by *F* for 4326 observed reflections with $I>2\sigma(I)$). All calculations were performed with SHELXS97 software suite.[14] The complete crystallographic data set was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1500119).

The Supplementary information file containing results of X-ray crystallographic analysis is available from the journal website at http://hgs.osi.lv.

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