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Functionalized 3H-1,2,3,4-triazaphosphole derivatives: Synthesis and structural characterization of novel low-coordinate phosphorus heterocycles

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ABSTRACT

The synthesis of novel functionalized 3*H*-1,2,3,4-triazaphosphole derivatives is presented, making use of the modular [3+2] dipolar cycloaddition reaction between an azide and a phosphaalkyne. These low-coordinate phosphorus heterocycles were prepared in high yield and could be characterized crystallographically. This strategy provides the possibility to access hitherto unknown chelating and potentially chiral P^O ligands based on triazaphospholes.

GRAPHICAL ABSTRACT



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Introduction

3,5-Disubstituted 3H-1,2,3,4-triazaphosphole derivatives of type **1** are the phosphorus analogs of the well-studied 1,4disubstituted 1,2,3-triazoles (**2**, Figure 1).¹ According to Nyulászi and Regitz, triazaphospholes have a conjugated π systems with a high degree of aromaticity and possess a rather high π -density at the phosphorus atom due to a significant N-C = P \leftrightarrow N⁺ = C-P⁻ conjugation.² These low-coordinate $\lambda^3 \sigma^2$ -phosphorus heterocycles can be prepared by a [3+2] cycloaddition of phosphaalkynes with azides, as demonstrated by Regitz et al. in 1984.^{3,4} In contrast to the Huisgen [3+2] reaction and the copper-catalyzed azide-alkyne cycloaddition (CuAAC, "click"-reaction), only one single regioisomer is thermally formed without the need of a catalyst.⁵ This provides the possibility to construct phosphorus containing triazole-derivatives in a rather facile manner, depending on the availability of the phosphaalkyne and the azide.

The incorporation of additional donor-functionalities within the heterocyclic framework is an important aspect for the design of triazaphosphole derivatives and their use in more applied research fields. As a matter of fact, coordination compounds containing chelating N^N ligands or different donorcombinations, such as N^O, P^O, or P^N, have been exploited to a large extend as functional components in electronic and luminescent materials and as precursor for homogeneous catalytic reactions.⁶ Consequently it could be interesting to create novel ligand systems based on polydentate triazaphospholes, in order to develop these interesting low-coordinate phosphorus heterocycles to their full potential. However, donor-functionalized triazaphospholes are very rare. Jones and co-worker described

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Figure 1. Selected 3H-1,2,3,4-triazaphospholes 1, 3-6 and triazole 2.

recently the access to tripodal P₃-ligands, such as compound **3**.⁷ The same group also reported on the facile assembly of trisand poly-(triazaphospholes), starting from the corresponding polyazides.⁸ Our group could recently demonstrate the access to new classes of chelating P,N as well as pincer-type P,N,P-hybrid ligands.^{9,10} The pyridyl-functionalized compounds **4** and **5** were easily prepared starting from (pyridylmethyl)azide, respectively, pyridotetrazole and 1-phospha-2-*tert*-butyl-acetylene. Similarily, starting from 2,6-bis(azidomethyl)pyridine, the pincer-type neutral P,N,P-ligand **6** could be obtained in high yields.

Inspired by these recent results and by our long-standing interest in low-coordinate phosphorus heterocycles, we set out to develop potentially chelating and also chiral triazaphospholes with different donor-combinations and our first achievements in this direction will be reported here.

Results and discussion

Derived from our recently reported pyridyl-functionalized P,Nhybrid ligand **4**, we aimed for the development of a functionalized triazaphosphole derivative containing a P^O donorcombination. At the same time, we were wondering whether we could implement a stereogenic center in the ligand backbone, in order to have the possibility to access also chiral triazaphospholes in the future. Therefore, we started from the commercially available 2-bromo-1-(p-toyl)ethane-1-one (7), which gave **8** after reaction with excess NaN₃ according to Scheme 1.¹¹



Scheme 1. Synthesis of (2-azido-1-(4-methylphenyl)ethoxy)trimethylsilane (10).



Scheme 2. Synthesis of functionalized triazaphospholes 13 and 14.

Reduction with excess NaBH₄ in ethanol led to the corresponding alcohol **9** in 88% isolated yield.¹² In future investigations, this reduction step could be performed with a chiral reagent, in order to obtain the entantiomerically pure alcohol.¹³ We further protected the OH-functionality with a TMS-group because phosphaalkynes are prone to nucleophilic attack. The racemic mixture of the TMS-protected compound **10** could be obtained in 85% isolated yield as a coloress oil.

All compounds were characterized by means of NMR spectroscopy as well as mass spectrometry.

10 was further converted in a [3 + 2] cycloaddition reaction with 1-phospha-2-*tert*-butyl-acetylene (${}^{t}BuC \equiv P$, 11) as well as with 1-phospha-2-trimethylsilyl-acetylene (Me₃SiC $\equiv P$, 12) to give regioselectively the corresponding 3H-1,2,3,4-triazaphosphole derivatives 13 and 14, according to Scheme 2. 13 and 14 were isolated as colorless solids in 86% and 97% yield, respectively.

Both compounds show the typical downfield shift of the phosphorus resonance in the ³¹P{¹H} NMR spectrum. While for the ^{*t*}Bu-substituted compound **13** the signal is observed at δ (ppm) = 174.0 (CD₂Cl₂), the SiMe₃-group in **14** has a rather large influence on the chemical shift, as the phosphorus-resonance is detected at δ (ppm) = 218.3 (CD₂Cl₂).

Because structural information on triazaphosphole derivatives are rare, we attempted a crystallographic characterization of the products and single crystals, suitable for X-ray crystal structure analysis, were obtained from concentrated solutions of 13 and 14 in pentane. Triazaphospholes 13 and 14 crystallized in the space group $P2_1/c$ and $P2_1/n$, respectively, and the molecular structures in the crystal, along with selected bond lengths and angles, are depicted in Figures 2 and 3. The graphical representation of 13 and 14 confirm the successful synthesis of these novel functionalized triazaphosphole-derivatives.



Figure 2. Molecular structure of **13** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)-C(1): 1.723(2), P(1)-N(1): 1.680(2), N(1)-N(2): 1.345(3), N(2)-N(3): 1.305(3), C(1)-C(11): 1.512(4), N(1)-C(2): 1.464(3), C(3)-O(1): 1.426(3), O(1)-Si(1): 1.655(2). N(1)-P(1)-C(1): 86.21(11).



Figure 3. Molecular structure of **14** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)-C(1): 1.713(2), P(1)-N(1): 1.673(2), N(1)-N(2): 1.343(3), N(2)-N(3): 1.309(3), C(1)-Si(2): 1.873(2), N(1)-C(2): 1.475(3), C(3)-O(1): 1.412(3), O(1)-Si(1): 1.656 (2). N(1)-P(1)-C(1): 87.48(11).

Although known for many years, only a few 3H-1,2,3,4triazaphospholes have so far been characterized crystallographically by Jones *et al.* and our group.^{7–10} All available structural parameters indicate significant conjugation within the phosphorus heterocycles. In case of 13 and 14 the P(1)-C(1) distances (1.723(2) Å and 1.713(2) Å) are slightly shorter than the P-C bond distances in 2,4,6-triarylphosphinines (\sim 1.75 Å).¹⁴ It thus lies between the values of a localized P = C double bond [(diphenylmethylene)-(mesityl)phosphine, $MesP = CPh_2$: 1.692 Å] and a P-C single bond (PPh₃: 1.83 Å¹⁵). The N-P-C angles are with 86.21(11) ° and 87.48(11)° almost close to 90° and differ significantly from the C-P-C angle in the aromatic six-membered phosphinines ($\sim 100^{\circ}$).¹⁶ The near 90° bond angle, which is characteristic for these phosphorus compounds, can apparently more easily be achieved in a planar pentagon (ideally 107°), than in a hexagon (ideally 120°). This can be explained by the fact that the lighter sp^2 -hybridized ring atoms strive for the trigonal planar arrangement. A similar effect contributes to the planarization of the σ^3 -P atom in polyphosphaphospholes.¹⁷ As suggested by Nyulászi and Regitz, all these observations are in line with a significant aromaticity within 1,2,3,4-triazaphospholes.

Experimental

General

All reactions were performed in an argon atmosphere by using Schlenk techniques, unless stated otherwise. All the glassware was dried prior to use by heating under vacuum. All the common chemicals were commercially available and purchased from AldrichChemical Co., ABCR, Alfa Aesar or Acros as well as Eurisol and were used as received. All solvents were dried and degased using standard techniques or used from Braun Solventsystems. The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Fa. JEOL ECX400 (400 MHz), Fa. JEOL ECP500 (500 MHz) or on Fa. BRUKER AVANCE500 (500 MHz), Fa. BRUKER AVANCE700 (700 MHz) spectrometers, and all the chemical shifts are reported relative to the residual resonance in the deuterated solvents. Infra-Red-spectra were obtained from Nicolet iS10 MIR FT-IR Spectrometer. ESI-TOF-Mass Spectrometry was performed on Agilent 6210 ESI-TOF, Agilent Technologies, Santa Clara, CA, USA, (5 μ L/min, 4 kV, 15 psi.). The voltage was optimized during the measurements for the max. abundance of [M+X]¹ signal (X: H, Na, K). The EI measurement was performed on a MAT 711, Varian Bremen, using an electron energy of 80eV. Me₃SiC=P, ^tBuC=P, 2-Azido-1-(4-methylphenyl)ethanone (**8**) and 2-Azido-1-(4methylphenyl)ethanol (**9**) were prepared according to the literature.^{11,12,18,19}

(2-Azido-1-(4-methylphenyl)ethoxy)trimethylsilane (10)

Compound 9 was dissolved in penante (65 mL) and 1,4diazabicyclo[2.2.2]octane (1.47 g, 13 mmol, 1.3 eq.) were added under stirring. Subsequently, trimethylsilylchloride (1.73 g, 16 mmol, 1.6 eq.) was added and the reaction mixture was stirred for overnight at room temperature. Diluted hydrochloric acid (1 N, 35 mL) was added and the mixture was neutralized with NaHCO₃. The organic phase was extracted three times with diethylether and the collected solutions were washed with water, brine and dried over MgSO₄. The solvent was removed in vacuo, yielding the product as a bright yellow oil (2.1 g, 8.4 mmol, 84%). IR (ATR, neat): $\tilde{v} =$ 2958 (N₃); 2095 (N₃); 1509; 1436; 1251; 812 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): $\delta = 0.03-0.11$ (m, 9H, Si(CH₃)₃), 2.34 (s, 3H, CH3), 3.05-3.12 (m, 1H, CH2N), 3.32-3.41 (m, 1H, CH₂N), 4.81 (dd, 1H, J = 8.5; 3.0 Hz, CHO(Si(CH₃)₃), 7.11– 7.23 (m, 4H, Ar-H) ppm. ¹³C{¹H}-NMR (101 MHz, CDCl₃): $\delta = 0.03$ (Si(CH₃)₃), 21.25 (CH₃), 58.69 (C-N3), 74.79 (C-OSi(CH3)3), 125.96 (Ar), 129.18 (Ar), 137.69 (Ar), 138.63 (Ar) ppm. MS (EI, 80 eV) m/z: 221.1 [M-N2]+• (calc.: 221. 1230).

5-(tert-Butyl)-3-(2-(p-tolyl)-2-[(trimethylsilyl)oxy]ethyl]-3H-1,2,3,4-triazaphosphole (13)

Azide 10 (0.895 g, 3.59 mmol, 1.0 eq.) was dissolved in toluene and an excess of ^tBuC \equiv P in toluene was added. Stirring was continued at room temperature for 5 h. Subsequently, the solvent and the residual phosphaalkyne were removed in vacuo and the crude product was recrystallized from pentane. The product could be obtained as white crystals (1.0 g, 2.9 mmol, 87%). IR (ATR, neat): $\tilde{v} = 2956$; 1252; 1088; 939; 841 cm⁻¹. ¹H-NMR (400 MHz, C_6D_6): $\delta = -0.13-0.16$ (m, 9H, Si(CH₃)₃), 1.50 $(d, J = 1.4 \text{ Hz}, 9\text{H}, {}^{t}\text{Bu}), 2.07 \text{ (s, 3H, CH}_{3}), 4.28-4.39 \text{ (m, 1H, })$ CH₂N), 4.46–4.55 (m, 1H, CH₂N), 5.04 (dd, 1H, J = 9.1; 3.4 Hz, 1H, CHO(Si(CH₃)₃), 6.94 (d, J = 7.8 Hz, 2H, Ar-H), 7.10 (d, J =8.1 Hz, 2H, Ar-H) ppm. ¹³C{¹H}-NMR (101 MHz, C₆D₆): δ = 0.29 (Si(CH₃)₃), 21.09 (CH₃), 31.84 (^tBu), 35.34 (^tBu), 60.09 (C-N₃), 75.24 (C-OSi(CH₃)₃), 126.10 (Ar), 129.46 (Ar), 137.74 (Ar), 138.81 (C = P) ppm. ³¹P{¹H}-NMR (162 MHz): δ = 174.03 ppm. Elemental analysis calcd (%) for C₁₇H₂₈N₃OPSi: C 57.29, N 11.88, H 7.81. Found: C 57.23, N 11.72, H 8.089.

5-(Trimethylsilyl)-3-(2-(p-tolyl)-2-[(trimethylsilyl)oxy]ethyl]-3H-1,2,3,4-triazaphosphole (14)

Prior to use, the concentration of Me₃SiC \equiv P in toluene was determined by means of ³¹P{¹H} NMR spectroscopy (105.7 mmol/L). This solution (25 mL, 1.0 eq.) was added to azide 10 (0.344 g, 1.38 mmol, 1.0 eq.) and stirring was continued for 1 h at room temperature, while the course of the reaction was monitored by means of ³¹P{¹H} NMR spectroscopy. The solvent and all volatiles were removed in vacuo and the product could be obtained as white solid (479.8 mg, 1.31 mmol, 97%). **IR (ATR, neat)**: $\tilde{v} = 2962$; 1259; 1091; 1016; 943 cm⁻¹. ¹H-**NMR (400 MHz, CD₂Cl₂)**: $\delta = -0.18 - 0.28$ (m, 9H, Si(CH₃)₃), 0.35-0.41 (m, 9H, O-Si(CH₃)₃), 2.32 (s, 3H, CH₃), 4.56-4.64 (m, 1H, CH₂N), 4.72-4.81 (m, 1H, CH₂N), 4.97 (dd, 1H, J = 9.0; 3.4 Hz, 1H, CHO(Si(CH₃)₃), 7.15 (d, J = 7.8 Hz, 2H, Ar-H), 7.25 (d, J = 7.9 Hz, 2H, Ar-H) ppm. ¹³C{¹H}-NMR (101 MHz, CD_2Cl_2 : $\delta = 0.76$ (O-Si(CH₃)₃), 0.80 (Si(CH₃)₃), 20.89 (CH₃), 59.65 (C-N3), 74.57 (C-OSi(CH₃)₃), 126.00 (Ar), 129.13 (Ar), 137.85 (Ar), 138.28 (C = P) ppm. ${}^{31}P{}^{1}H$ -NMR (162 MHz): $\delta = 218.32$ ppm.

X-ray crystal structure determination of 13

Crystals suitable for X-ray diffraction were obtained by cooling slowly down a hot saturated solution of 13 in pentane. Crystallographic data: $C_{17}H_{28}N_3OPSi$; Fw = 349.48; 0.35 mm × 0.04 mm \times 0.02 mm; colorless needle, monoclinic; $P2_1/c$; a =6.2652(2), b = 16.0712(5), c = 20.0483(6) Å; $\alpha = 90^{\circ}, \beta = 96.058$ (2), $\gamma = 90^{\circ}$; $V = 2007.38(11) \text{ Å}^3$; Z = 4; $Dx = 1.156 \text{ gcm}^{-3}$; $\mu = 1.837 \text{ mm}^{-1}$. 12965 reflections were measured by using a SAINT v8.34A (Bruker, 2013)²⁰ diffractometer (CuK α radiation; $\lambda = 1.54178$ Å) up to a resolution of $(\sin\theta/\lambda)_{max} = 0.60$ $Å^{-1}$ at a temperature of 100.07 K. 2991 reflections were unique $(R_{\rm int} = 0.049)$. The structures were solved with SHELXS-2013²¹ by using direct methods and refined with SHELXL-2013²¹ on F2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 215 parameter were refined with one restraint. $R_1 = 0.050$ for 2991 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.125$ for 3499 reflections, S = 1.112, residual electron density was between -0.30 and 0.45eÅ⁻³. Geometry calculations and checks for higher symmetry were performed with the PLATON program²²

CCDC-1424047 (13) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray crystal structure determination of 14

Crystals suitable for X-ray diffraction were obtained by cooling slowly down a hot saturated solution of **14** in pentane. *Crystallographic data*: C₁₆H₂₈N₃OPSi₂; *Fw* = 365.56; 0.35 mm × 0.04 mm × 0.02 mm; colorless needle, monoclinic; P2₁/*n*; *a* = 6.1929(5), *b* = 3.452(3), *c* = 15.0751(12)Å; α = 90°, β = 97.705(3), γ = 90°; *V* = 2169.7(3) Å³; *Z* = 4; *Dx* = 1.119 gcm⁻³; μ = 0.244 mm⁻¹. 14570 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (MoK α radiation; $\lambda = 0.71073$ Å) up to a resolution of $(\sin\theta/\lambda)_{max} = 0.69$ Å⁻¹ at a temperature of 210.0 K. 2991 reflections were unique ($R_{int} = 0.102$). The structures were solved with SHELXS-2013²¹ by using direct methods and refined with SHELXL-2013²¹ on F2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 215 parameter were refined with one restraint. $R_1 = 0.050$ for 2736 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.102$ for 5783 reflections, S = 0.881, residual electron density was between -0.20 and 0.21eÅ⁻³. Geometry calculations and checks for higher symmetry were performed with the PLATON program²²

CCDC- 1424046 (14) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

We have presented the access to novel functionalized 3H-1,2,3,4-triazaphosphole derivatives making use of the modular [3 + 2] dipolar cycloaddition reaction between an azide and a phosphaalkyne. The TMS-protected 3(1-methyl-4-[1-[trimethylsilyl)oxy]ethyl]phenyl-1,2,3,4-triazaphospholes have been prepared in high yield and were characterized crystallographically. These compounds can be used as a starting point for the preparation of chelating and chiral P^O ligands based on low-coordinate phosphorus heterocycles for applications in the field of asymmetric homogeneous catalysis. Experiments to deprotect the OH-functionality and to start from enantiomerically pure building blocks are currently performed in our laboratories and will be reported elsewhere.

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