π-Excess σ²*P*,*O* Hybrid Ligands: Synthesis of the First 4-Methoxy-1*H*-1,3-benzazaphospholes

Bhaskar R. Aluri,[a] Peter G. Jones,[b] Ina Dix,[c,1] Joachim W. Heinicke*[a]

[a] Institut für Biochemie, Anorganische Chemie, Ernst-Moritz-Arndt-Universität Greifswald, 17487 Greifswald, Germany
Fax +49(3834)864377; E-mail: heinicke@uni-greifswald.de

[b] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, 38023 Braunschweig, Germany

[c] Institut für Anorganische Chemie, Universität Göttingen, Tammannstr. 4, 37077 Göttingen, Germany

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Abstract: The synthesis of the first 4-methoxy-substituted 1,3-benzazaphosphole was accomplished by using a *C*,*O*-dilithium intermediate generated from *N*-(3-methoxyphenyl)-2,2-dimethylpropanamide and butyllithium. This intermediate was subjected either to direct phosphonylation or to a bromination and phosphonylation sequence; subsequent reductive cyclization with excess lithium aluminum hydride led to the desired product. In addition, *N*-(2,2-dimethylpropyl)-3-methoxy-2-phosphinoaniline, formed in a side reaction, was cyclized with (dimethoxymethyl)dimethylamine to give 1-(2,2-dimethylpropyl)-4-methoxy-1*H*-1,3-benzazaphosphole. The behavior of these +*M*-substituted π-excess aromatic σ²*P*-heterocycles towards moisture is reported, together with their ^{1}H, ^{13}C, and ^{31}P solution NMR spectra and a crystal-structure analysis. The new compounds represent potential σ²*P*,*O* hybrid or chelate ligands with a high π-density at the phosphorus atom.

Key words: lithiation, cross-coupling, phosphorus, ring closure, heterocycles, ligands

1*H*-1,3-Azaphospholes constitute a particular type of heterocycles containing dicoordinated phosphorus (σ²P).[2–4] They are aromatically stabilized by delocalization of 6 π-electrons within the five-membered ring,[5] and they display a high π-density at phosphorus as a result of interplay between the –*I* and +*M* effects of the tricoordinated nitrogen atom (σ³*N*) conjugated to the phosphorus atom. The high π-density is reflected in much higher upfield phosphorus resonances compared with phosphinines or azaphospholes with P–N bonds;[6] it is also reflected in the reactivity of such compounds, studied mainly in the case of benzo-fused 1,3-azaphospholes. A particular feature of these compounds is their reduced tendency to add organolithium compounds at the P=C double bond in polar media, thereby permitting lithiation at the NH or 2-CH positions and subsequent use of the resulting P=C–NLi and P=CLi–NR reagents in substitution reactions.[7,8] Another feature of the compounds is their μ-*P* or bent η¹-*P* coordination to d¹⁰ transition-metal cations outside the ring plane, with contributions from π-donor bonds.[9] In contrast, phosphinines do not form isolable 2-lithio species and preferentially adopt in-plane η¹–σ-coordination towards d¹⁰ transition-metal cations, except in cases where steric distortion occurs[10] or, as shown recently, where there is a +*M* substituent in the position *ortho* to the σ²P moiety. Copper(I) complexes[11] of 2-hydroxyphosphinines[12] also display μ or bent coordination, as well as the usual in-plane σ-coordination mode.

For further studies on the coordination behavior of σ²*P*-heterocycles with a high π-density at phosphorus, benzazaphosphole ligands with a greater abundance of π-electrons are desirable. 2-(Dimethylamino)- and 2-(phenylamino)-1,3-benzazaphospholes,[13] which show particularly strong π-donation towards σ²P together with unusually high upfield phosphorus chemical shifts (δ = −4.6 and 7.6 ppm, respectively), are known. These might be capable of forming four-membered κ*P*,κ*N* chelate complexes or eight-membered dimers thereof. However, such chelate rings are not favored in the case of weakly coordinating σ²*P* ligands. Thus, di-*tert*-butylphosphino-1,3-benzazaphospholes preferentially adopt other coordination modes to late-transition-metal ions.[14] However, sterically more suitable six-membered 2-[(2-diphenylphosphino)phenyl]-1,3-benzazaphosphole–κ²*P*,*P*′ chelate complexes are sufficiently stable to permit their isolation and structural characterization.[9,15] Therefore, the introduction of a +*M* substituent in a position *ortho* to phosphorus to increase the π-density at σ²P and, at least formally, to permit the formation of five-membered chelate rings, appeared to be attractive. We report here the synthesis and structural characterization of the first 4-methoxy-substituted 1,3-benzazaphospholes, which are potential candidates for preparing late-transition-metal complexes with coordination at σ²P and O.

A short synthesis by a directed *ortho*-lithiation strategy starting from *m*-anisidine was developed.[16] Pivaloylation provided the 3-methoxy-substituted anilide **1** (Scheme 1), which is known to undergo rapid and regiospecific *ortho*-lithiation with 2.5 equivalents of butyllithium in tetrahydrofuran at 0 °C to give the intermediate **2**, which subsequently gives good yields of coupling products with iodomethane, dimethyl disulfide, benzaldehyde, *N*,*N*-dimethylformamide, fluorobenzonitrile, carbon dioxide, or 1,2-dibromoethane.[17] Coupling reactions with organo-substituted halides of hetero-elements, however, have not yet been reported. A test reaction of lithio compound **2** with excess chlorotrimethylsilane (2.5 equivalents to trap lithium as lithium chloride) gave the silylated amide **3** in 75% yield.

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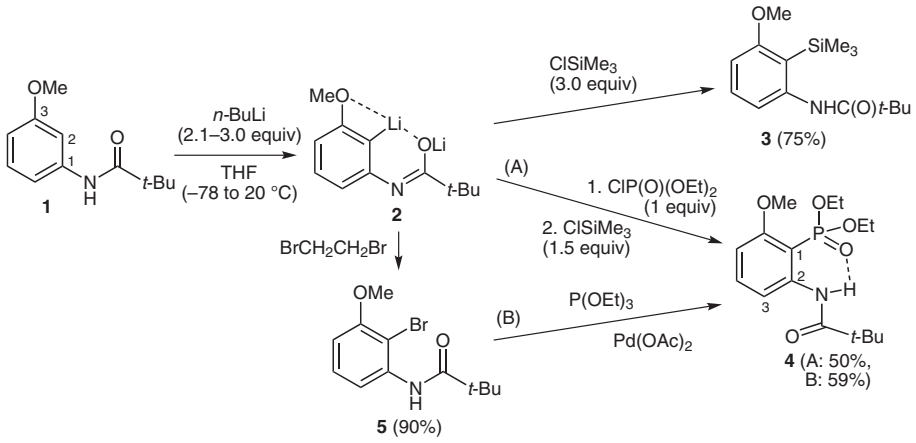
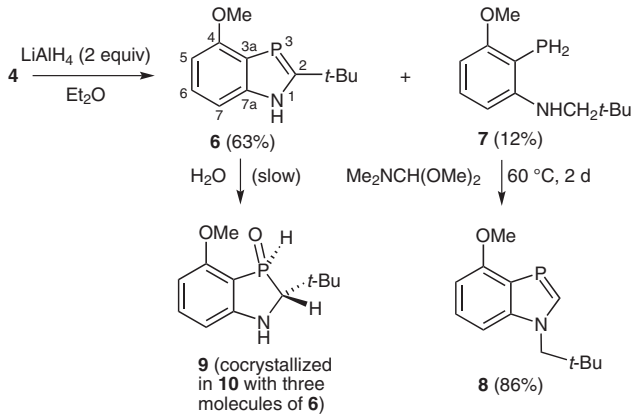


Scheme 1 Reactivity of the *ortho*-*C*,*O*-dilithium reagent **2**

Trimethylsilylation of the lithiated imidate group was not observed after workup, even in the absence of protic solvents, which hints at extreme sensitivity to any traces of moisture. Aqueous workup also cleaved the *C*-trimethylsilyl group. The electrophilic protolysis of the aryl–Si bond in positions *ortho* or *para* to an OR group is known;[18] in this case, it was further facilitated by the presence of the additional amide group in the second *ortho*-position. Coupling of the *C*,*O*-dilithium reagent **2** with diethyl chlorophosphate was performed in a 1:1 molar ratio. After 15 hours at room temperature, excess chloro(trimethyl)silane (1.5 equiv) was added to couple with the remaining *C*-Li and *O*-Li species. NMR monitoring after one hour showed that an *o*-phosphonoanilide was the main product ($\delta^{31}P = 19.5$ ppm); this was accompanied by two other phosphorus compounds with ^{31}P resonances at $\delta = 16.2$ and -9.1 ppm (relative intensities 42:29:19), together with a small amount of unconverted diethyl chlorophosphate. After two days at room temperature, the amount of the *o*-phosphonoanilide increased further at the expense of the unidentified side products (relative intensities 71:8:12). Monitoring of the trimethylsilyl groups by proton NMR revealed the presence of three trimethylsilyloxy signals and a downfield resonance at $\delta = 0.31$ ppm, possibly from a *C*–$SiMe_3$ group. Aqueous workup was chosen to achieve desilylation, giving phosphonate **4** and amide **1** as the main products in a molar ratio of 2:1. Purification by column chromatography on silica gel gave pure phosphonate **4** in 50% yield.

An alternative route to phosphonate **4** involved bromination of lithio compound **2** with a slight excess of 1,2-dibromoethane[17c] and phosphonylation of the resulting bromo amide **5** by heating with excess triethyl phosphite in the presence of 5 mol% of palladium(II) acetate. This protocol initially gave a palladium(0) triethyl phosphite complex that subsequently induced a transition-metal-catalyzed Michaelis–Arbuzov reaction, also known as the Tavs reaction, after its inventor.[19] Although coupling of amide **5** with triethyl phosphite to form the phosphonate **4** required harsh conditions (200 °C for 1 h), the pure product was isolated in 59% yield after column chromatography.

Direct treatment of phosphonate **4** with excess lithium aluminum hydride gave the desired 4-methoxy-1,3-benzazaphosphole **6**, together with a minor amount of phosphine **7** (molar ratio 2:1 by ^1H NMR integration). Whereas the formation of benzazaphosphole **6** is attributed to preferential reduction of the diethoxyphosphoryl group and subsequent cyclization by intramolecular attack of the phosphine or lithiophosphine on the N=C–OLi group,[20] phosphine **7** is formed by concomitant reduction of the diethoxyphosphoryl and the amide groups. Phosphine **7** was separated by high-vacuum distillation and subsequently cyclized by gentle heating with (dimethoxymethyl)dimethylamine to give the benzazaphosphole **8** (Scheme 2). When treated with dilute aqueous sulfuric acid to separate basic nitrogenous impurities, compound **6** underwent slow addition of water, as previously observed for 2-*tert*-butyl-*1H*-1,3-benzazaphosphole.[21] Slow concentration of a sample containing the water adduct **9** along with unconverted benzazaphosphole **6** in benzene-d_6 resulted in cocrystallization to give single crystals of an adduct **10**, consisting of the two molecules **9** and **6** in a 1:3 molar ratio together with two molecules of benzene-d_6. In contrast to **6**, benzazaphosphole **8** was stable to dilute aqueous sulfuric acid. This showed that the 4-methoxy group is not involved in the addition of water, although it might attract water by means of $O_{Me}\cdots H_2O$ interactions adjacent to σ^2P. The addition of water to the P=C bond, with subsequent isomerization to the secondary phosphine oxide **9**, is connected with the 2-*tert*-butyl and NH substitution pattern. This can be explained in terms of enhanced basicity of the phosphorus atom, caused by the *+I* effect of the *tert*-butyl group and by protonation of phosphorus, leading to rapid addition of water, as observed after P-alkylation or P-arylation of 1,3-benzazaphospholes.[22]



Scheme 2 Synthesis of 4-methoxy-1,3-benzazaphospholes

Elucidation of the structures of the new compounds **3**–**8** is based on conclusive multinuclear solution NMR spectra, supplemented by analytical or high-resolution mass spectrometry data. The characteristic shift ranges, the coupling patterns, and the position-dependent J_{PH} and J_{PC} coupling constants[3,7,8,20–23] were used to assign the ^{1}H and ^{13}C NMR signals and thereby confirm the structures. The phosphorus chemical shifts characterize the compound type through the specific shift ranges for diethyl arylphosphonates, primary arylphosphanes, and benzazaphospholes. The increased shielding at phosphorus in the 4-methoxy-substituted benzazaphospholes **6** and **8** (δ = 56.8 and 61.5 ppm) compared with 2-*tert*-butyl- and 1-neopentyl-1,3-benzazaphospholes lacking a methoxy group (δ = 65.1[21] and 70.8 ppm[8b]), corresponding to upfield shifts Δδ = −8.3 and −9.3 ppm, is attributable to the +*M* effect of the methoxy group in the position *ortho* to phosphorus and to the increased π-density at σ²P, rather than to steric screening by the methoxy group. This corresponds to the more significant electronic effects of N-substituents compared to the steric screening by substituents at the carbon atom of the P=C bond. Thus, whereas 2-alkyl or 2-phenyl groups cause only small upfield or downfield shifts (Δδ ≈ ±3 ppm),[7a] more remote *N*-adamantyl or *N*-mesityl groups, which affect the N-donor ability, induce upfield or downfield shifts of Δδ ≈ ± 6 ppm).[8b] Also noteworthy is the strong downfield shift of the NH proton resonance in phosphonate **4**, indicative of the presence of an intramolecular N–H···O(=P) hydrogen bond, as observed (and confirmed by X-ray crystal structures) for other *N*-secondary *o*-phosphonoanilides.[23]

Detailed structural data of **6** and its water adduct **9** were provided by a crystal structure analysis of the adduct **10** (Figure 1), which crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains three molecules of **6** and one molecule of **9**, arranged in a chain **6**···**6**···**6**···**9** connected by hydrogen bonds, and in addition two benzene-d_6 molecules. All hydrogen atoms at N, P3, and C2 were identified in difference syntheses. Despite the presence of rather long HP distances [3.10(2) to 3.29(2) Å], the existence of three-center hydrogen bonds [N–H 0.82(2) to 0.85(2), H···OMe 2.237(19) to 2.32(2), H···P 3.10(2) to 3.29(2) Å] between the NH function and OMe and σ²P as proton acceptors is feasible. The phosphine oxide **9** terminates this chain at the NH end of the asymmetric unit with a hydrogen bond to the O=P function [N–H 0.87(2), H···O 1.93(2) Å, N–H···O 169.3(18)°]. The NH function of benzazaphosphole **9** makes only a long H···P contact, and the methoxy oxygen at the other end of the chain accepts no classical hydrogen bond, so that the chains can be regarded as isolated. The bond lengths and angles in the benzazaphosphole **6** are similar to those in 2-*tert*-butyl-1,3-benzazaphosphole,[7b] except that the C2–P3 bonds are slightly longer (by 0.02 to 0.03 Å). For **9**, the C2–P3 bond is longer as a result of sp³-hybridization of the carbon atom, but the C3A–P3 bond is shorter than that in **6** by ~0.02 Å, indicating a strong bond between the sp³P and the polar P=O ↔ P⁺–O⁻ group. The C3A–P3–C2 angle is larger in **9** than in **6**, and the P3–C2–N1 angle is smaller; these differences are also associated with the difference in hybridization at P3 and C2. The oxygen atom on the phosphorus is arranged in a position *trans* to the 2-*tert*-butyl group, with a 2*S*,3*S*-configuration (the overall structure is a racemate).

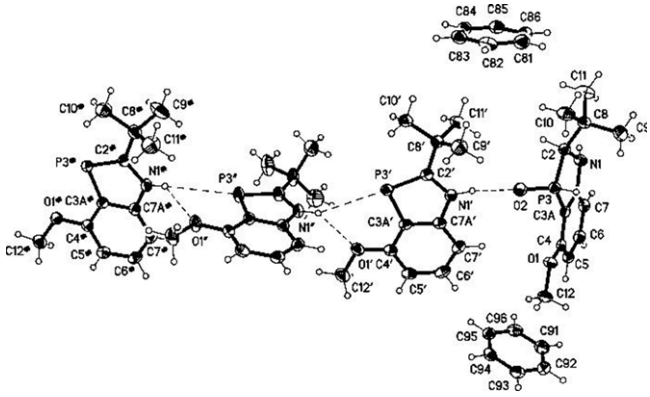


Figure 1 Crystal structure of adduct **10**; the asymmetric unit consists of three molecules of **6** and one of **9**, together with two of C_6D_6. Ellipsoids represent 50% probability levels. Hydrogen bonds are indicated by dashed lines. Selected bond lengths (Å): **6**: P3′–C2′ 1.7430(17), P3′–C3A′ 1.7915(15), C2′–N1′ 1.364(2), N1′–C7A′ 1.371(2), C3A′–C7A′ 1.400(2); P3″–C2″ 1.7361(16), P3″–C3A″ 1.7836(16), C2″–N1″ 1.362(2), N1″–C7A″ 1.375(2), C3A″–C7A″ 1.401(2); P3#–C2# 1.7321(17), P3#–C3A# 1.7887(15), C2#–N1# 1.369(2), N1#–C7A# 1.370(2), C3A#–C7A# 1.401(2); C2′–P3′–C3A′ 88.56(7), N1′–C2′–P3′ 113.05(12); C2″–P3″–C3A″ 88.71(7), N1″–C2″–P3″ 113.00(12); C2#–P3#–C3A# 88.79(8), N1#–C2#–P3# 112.94(12); **9**: P3–O2 1.4865(12), P3–C2 1.8510(16), P3–C3A 1.7719(15), C2–N1 1.470(2), N1–C7A 1.383(2), C3A–C7A 1.395(2); C2–P3–C3A 93.06(7), N1–C2–P3 104.52(10).

In conclusion, 4-alkoxy-2-*tert*-butyl-*1H*-1,3-benzazaphospholes can be synthesized via *C*,*O*-dilithium reagents generated from *N*-(3-alkoxyphenyl)pivalamides, followed by direct phosphonylation with diethyl chlorophosphate or bromination and subsequent palladium-catalyzed Tavs coupling with triethyl phosphite. The resulting phosphonate is finally reduced with excess lithium aluminum hydride. In the cases of competing or preferred concomitant reduction of the amide group, *N*-secondary 3-alkoxy-

2-phosphanylanilines are formed, which undergo cyclocondensation with suitable carboxylic acid derivatives to give the corresponding NCH_2R-substituted 4-alkoxy-1,3-benzazaphospholes. Upfield shifts of the ^{31}P NMR signals induced by the 4-methoxy group (in comparison with 4-H) confirmed the expected increase in π-density at phosphorus as a result of the +*M* effect of the substituent in the *ortho*-position. A knowledge of a route to 4-alkoxy-1,3-benzazaphospholes paves the way for coordination chemical studies with π-rich σ^2P,O benzazaphosphole hybrid or chelate ligands and, in particular, to investigations of whether complexes with π-donor-bond contributions to late transition metals, stabilized by chelate formation, are possible.

NMR spectra were recorded on a Bruker Avance II 300 multinuclear Fourier-transform spectrometer at 300.1 (^{1}H), 75.5 (^{13}C), or 121.5 (^{31}P) MHz. Shift references were the TMS or solvent signals, calibrated with TMS for the ^{1}H and ^{13}C NMR spectra or H_3PO_4 (85%) for the ^{31}P NMR spectra. Assignment numbers follow the nomenclature, and are indicated in Schemes 1 and 2. Coupling constants refer to J_{HH} in ^{1}H NMR spectra and to J_{PC} in ^{13}C NMR spectra. Low-resolution mass spectra were recorded on an AMD40 (Maurer) instrument. HRMS (ESI) measurements were carried out in Göttingen with a 7T Fourier-transform ion cyclotron resonance mass spectrometer (APEX IV; Bruker Daltonics). Melting points (uncorrected) were determined with a Sanyo Gallenkamp melting-point apparatus. The experiments were carried out under dry N_2 in carefully dried and freshly distilled solvents. Commercial chemicals were used as purchased.

N-(3-Methoxyphenyl)-2,2-dimethylpropanamide (**1**) was synthesized by slightly modified version of a previously reported method,[17] from 3-$MeOC_6H_4NH_2$, *t*-BuCOCl, and Et_3N as auxiliary base in Et_2O; yield: 83%; mp 116–118 °C.

_N_-(2-Bromo-3-methoxyphenyl)-2,2-dimethylpropanamide (5)

This was obtained by a known route,[17c] and purified by column chromatography (silica gel, 30% CH_2Cl_2–hexanes) to give a yellow oil; yield: 3.7 g (90%). ^{1}H and mass spectroscopic data were in accordance with known values.

^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 27.52 (C*Me*$_3$), 40.23 (*C*$_q$Me$_3$), 56.30 (OMe), 103.08 (C$_q$-2), 106.87 (CH-4), 113.64 (CH-6), 128.37 (CH-5), 136.99 (C$_q$-1), 155.76 (C$_q$-3), 176.64 (C=O).

_N_-[3-Methoxy-2-(trimethylsilyl)phenyl]-2,2-dimethylpropanamide (3)

A 15% solution of BuLi in hexane (16.5 mL, 26.0 mmol) was added dropwise to a solution of amide **1** (1.80 g, 8.68 mmol) in THF (15 mL) at −78 °C. The mixture was stirred at r.t. overnight then cooled to −78 °C and TMSCl (3.3 mL, 26.0 mmol) was added. The mixture was kept for 1 d at r.t. and then THF was removed under vacuum. Et_2O (10 mL) was added and the precipitate was filtered off and washed thoroughly with Et_2O. The organic phases were combined and concentrated under vacuum to give a brown oil that was crystallized from a small amount of THF to give moisture-sensitive colorless needles; yield: 1.8 g (75%).

IR (KBr): 3304, 2965, 1645, 1503, 1242, 849 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 9 H, $SiMe_3$), 1.17 (s, 9 H, CH_3), 3.62 (s, 3 H, OCH_3), 6.51 (dd, ^3J = 7.7, ^4J = 1.3 Hz, 1 H, H-4), 7.15 (t, ^3J = 7.9 Hz, 1 H, H-5), 7.20 (dd, ^3J = 8.1, ^4J = 1.3 Hz, 1 H, H-6), 7.21 (br s, NH).

^{13}C{^{1}H} and DEPT-135 NMR ($CDCl_3$): δ = 1.91 ($SiMe_3$), 27.65 (C*Me*$_3$), 39.45 (*C*$_q$Me$_3$), 55.18 (OCH_3), 107.06 (CH-4), 117.97 (CH-6), 119.70 (C$_q$-2), 130.78 (CH-5), 143.23 (C$_q$-1), 164.89 (C$_q$-3), 176.81 (CO).

MS (EI, 70 eV, 130 °C): *m/z* (%) = 279 (2.4) [M$^+$], 265 (17), 264 (100), 57 (36).

Anal. Calcd for $C_{15}H_{25}NO_2Si$ (279.45): C, 64.17; H, 9.02; N, 5.01. Found: C, 63.96; H, 8.93; N, 4.93.

Diethyl {2-[(2,2-Dimethylpropanoyl)amino]-6-methoxyphenyl}phosphonate (4)

Method A: A 1.6 M solution of BuLi in hexane (13.6 mL, 21.8 mmol) was cooled to −70 °C and rapidly added to a cold (−70 °C) solution of amide **1** (2.15 g, 10.4 mmol) in THF (20 mL). The mixture was slowly warmed to 0–5 °C and stirring was continued at this temperature for 2 h. The mixture was cooled to −70 °C and $(EtO)_2P(=O)Cl$ (1.58 mL, 10.9 mmol) was added. The mixture was then slowly warmed to r.t. and kept for 15 h to complete the conversion, TMSCl (2.8 mL, 21.8 mmol) was then added at −45 °C, and the mixture was slowly warmed to 30 °C for 1 h. The progress of the reaction was monitored by NMR, and the measurements were repeated after 2 d (see above). THF was removed under vacuum and replaced with Et_2O (20 mL). LiCl was filtered off and washed with Et_2O (10 mL). The filtrate was treated with H_2O, and the Et_2O layer was separated and dried (Na_2SO_4). NMR of the crude product indicated the presence of product **4** and the starting material **1** in a molar ratio of 2:1, together with minor impurities (δ^{31}P = 18.7 and 9.0 ppm). Separation of **1** ($R_f \approx 0.35$) and the minor impurities from **4** ($R_f \approx 0.1$) by column chromatography (silica gel, 15% EtOAc–pentane) gave pure **4** as viscous pale-yellow oil; yield: 1.8 g (50%). The NMR data agreed well with those for the product prepared by method B.

Method B: A mixture of amide **5** (500 mg, 1.75 mmol), $Pd(OAc)_2$ (20 mg, 5.0 mol%), and $P(OEt)_3$ (0.32 mL, 1.93 mmol) was heated for 1 h at 200 °C in a distillation apparatus. The crude product was purified by column chromatography (silica gel, 10% EtOAc–hexane); yield: 355 mg (59%).

^{1}H NMR ($CDCl_3$): δ = 1.31 (t, ^3J = 7.1 Hz, 6 H, CH_3), 1.33 (s, 9 H, *t*-Bu), 3.86 (s, 3 H, OCH_3), 3.99–4.16 (m, 4 H, OCH_2), 6.63 (br dd, ^3J = 8.0, $^4J_{PH}$ = 5.3 Hz, ^4J small, 1 H, H-5), 7.46 (t, ^3J = 8.4 Hz, 1 H, H-4), 8.42 (ddd, ^3J = 8.6, $^4J_{PH}$ = 5.8, ^4J = 0.6 Hz, 1 H, H-3), 11.70 (br s, NH).

^{13}C{^{1}H} DEPT135 NMR ($CDCl_3$): δ = 16.25 (d, ^3J = 6.6 Hz, OCH_2CH_3), 27.51 (s, C*Me*$_3$), 40.44 (s, *C*$_q$Me$_3$), 56.05 (s, OCH_3), 62.54 (d, ^2J = 5.1 Hz, OCH_2), 101.11 (d, ^1J = 175.5 Hz, C$_q$-1), 105.50 (d, ^3J = 8.4 Hz, CH-3), 113.36 (d, ^3J = 11.6 Hz, CH-5), 135.01 (s, CH-4), 145.70 (d, ^2J = 5.6 Hz, C$_q$-2), 162.21 (C$_q$-6), 178.29 (C=O).

^{31}P{^{1}H} NMR ($CDCl_3$): δ = 20.0.

MS (EI, 70 eV, 130 °C): *m/z* (%) = 343 (19) [M$^+$], 286 (100), 258 (27), 230 (51), 57 (35).

HRMS (ESI in MeOH–H_2O and HCO_2H): *m/z* calcd for $C_{16}H_{26}NO_5P$ (343.36): [M + H]$^+$ 344.16214, [M + Na]$^+$ 366.14408; found: 344.16208, 366.14396.

2-*tert*-Butyl-4-methoxy-*1H*-1,3-benzazaphosphole (6) and _N_-(2,2-Dimethylpropyl)-3-methoxy-2-phosphinoaniline (7)

A solution of phosphonate **4** (2.45 g, 7.13 mmol) in Et_2O (30 mL) was added dropwise at 0 °C to $LiAlH_4$ tablets (812 mg, 21.4 mmol) stirred in Et_2O (15 mL). Stirring was continued at r.t. for 2 d and then the mixture was hydrolyzed at 0 °C by dropwise addition of degassed H_2O until evolution of H_2 ceased. The mixture was filtered and the solid residue was thoroughly washed with Et_2O (30 mL). The filtrate was dried (Na_2SO_4), separated, and concentrated under vacuum. NMR monitoring of the resulting solid showed signals for **6** as the major component and **7** as a minor component. An attempt to separate **6** by extraction of **7** with cold 10% aq H_2SO_4 did not give pure **6**, but led to single crystals of **10** containing **6** cocrystallized with **9** in a molar ratio 3:1 (crystal data below; for selected bond lengths and angles, see Figure 1). The main part of the crude product was then heated under high vacuum (10^{-5} mbar) at a bath tempera-

ture of 50 °C, and the more volatile **7** was separated by distillation. The residue was almost pure **6** (≥95 mol%, based on *t*-Bu integration), which solidified to give a colorless solid; corrected yield: 1.0 g (63%); mp 158 °C.

The distillate consisted of slightly contaminated colorless liquid **7** [yield: ~200 mg (~12%)], which was used in the reaction with (dimethoxymethyl)dimethylamine without further purification.

6

^{1}H NMR (C_6D_6): δ = 1.50 (d, ^4J = 1.2 Hz, 9 H, CH_3), 3.97 (s, 3 H, OCH_3), 6.51 (ddd, ^3J = 7.5, $^4J_{PH}$ = 3.3, ^4J = 0.7 Hz, 1 H, H-7), 7.17 (dt, ^3J = 8.2, $^4J_{PH}$ = 1.5, ^4J = 0.7 Hz, 1 H, H-5), 7.24 (t, ^3J = 8.2, 7.5 Hz, 1 H, H-6), 9.10 (br s, NH).

^{13}C{^{1}H} (DEPT) NMR (C_6D_6): δ = 31.42 (d, ^3J = 9.0 Hz, C*Me*$_3$), 35.73 (d, ^2J = 13.0 Hz, C_qMe$_3$), 55.33 (s, OCH_3), 99.32 (d, ^3J = 6.3 Hz, CH-5), 106.24 (s, CH-7), 125.59 (d, ^4J = 2.0 Hz, CH-6), 129.86 (d, ^1J = 42.1 Hz, C_q-3a), 143.76 (d, ^2J = 5.1 Hz, C_q-7a), 159.64 (d, ^2J = 10.8 Hz, C_q-4), 189.97 (d, ^1J = 57.6 Hz, C_q-2).

^{31}P{^{1}H} NMR (C_6D_6): δ = 56.8.

MS (EI, 70 eV, 140 °C): *m/z* (%) = 222 (11), 221 (69) [M$^+$], 207 (13), 206 (100), 182 (70), 168 (26).

HRMS (ESI in MeOH–H_2O, HCO_2H): *m/z* calcd for $C_{12}H_{16}NOP$ (221.24): [M + H]$^+$ 222.10423, [M + Na]$^+$ 244.08617; found: 222.10434, 244.08631.

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^{1}H NMR (C_6D_6): δ = 0.85 (s, 9 H, CH_3), 2.76 (s, 2 H, NCH_2), 3.39 (s, 3 H, OCH_3), 3.64 (d, ^1J = 205.3 Hz, PH_2), 4.20 (br s, NH), 6.14 (dd, ^3J = 8.2, $^4J_{PH}$ + ^4J = 1.8 Hz, 1 H, H-4 or H-6), 6.35 (dd, ^3J = 8.2, $^4J_{PH}$ + ^4J = 2.6 Hz, 1 H, H-4 or H-6), 7.18 (t, ^3J = 8.2 Hz 1 H, H-5).

^{13}C{^{1}H} and DEPT135 NMR (C_6D_6): δ = 28.30 (s, C*Me*$_3$), 32.49 (s, C_qMe$_3$), 56.02 (s, OCH_3), 56.76 (s, NCH_2), 99.20 (d, ^1J = 11.6 Hz, C_q-2), 100.44 (d, ^3J = 0.7 Hz, CH-6 or 4), 105.13 (d, ^3J = 1.5 Hz, CH-4 or 6), 131.43 (s, CH-5), 153.50 (d, ^2J = 8.0 Hz, C_q-1), 163.10 (d, ^2J = 5.4 Hz, C_q-3).

^{31}P{^{1}H} NMR (C_6D_6): δ = –178.3.

MS (EI, 70 eV): *m/z* (%) = 226 (7), 225 (44) [M$^+$], 168 (100), 166 (18), 136 (27).

1-(2,2-Dimethylpropyl)-4-methoxy-1*H*-1,3-benzazaphosphole (8)

Phosphine **7** (150 mg, 0.67 mmol) and $Me_2NCH(OMe)_2$ (0.09 mL, 0.73 mmol) were heated at 60 °C for 2 d. Excess $Me_2NCH(OMe)_2$ was removed in vacuum, and the residue was dissolved in Et_2O (10 mL). The soln was washed with cold degassed 10% aq H_2SO_4 (2 mL). The Et_2O layer was washed with degassed H_2O (2 × 2 mL), dried (Na_2SO_4), and separated from the drying agent. Removal of the solvent under vacuum gave an oily product contaminated with a minor impurity (≤10%); yield: 135 mg (corrected yield: 80%).

^{1}H NMR ($CDCl_3$): δ = 1.02 (s, 9 H, CMe_3), 4.01 (s, 3 H, OCH_3), 4.09 (s, 2 H, NCH_2), 6.55 (dd br, ^3J = 7.5, Hz, $^4J_{PH}$ = 3.4 Hz, 1 H, H-5), 7.22 (d br, ^3J = 8.6 Hz, 1 H, H-7), 7.31 (t br, ^3J = 8.5, 7.5 Hz, 1 H, H-6), 8.37 (d, $^2J_{PH}$ = 38.4 Hz, 1 H, H-2).

^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 28.34 (s, CH_3), 34.55 (d, ^4J = 0.8 Hz, *C*Me$_3$), 55.50 (s, OCH_3), 61.20 (d, ^3J = 3.0 Hz, NCH_2), 98.92 (d, ^3J = 6.6 Hz, CH-5), 106.83 (s, CH-7), 125.61 (d, ^4J = 2.3 Hz, H-6), 131.65 (d, ^1J = 40.3 Hz, C_q-3a), 145.14 (d, ^2J = 5.5 Hz, C_q-7a), 159.81 (d, ^2J = 10.6 Hz, C_q-4), 162.15 (d, ^1J = 51.4 Hz, CH-2).

^{31}P{^{1}H} NMR ($CDCl_3$): δ = 61.5.

MS (EI, 70 eV, 100 °C): *m/z* (%) = 236 (15) [M$^+$], 236 (100) [M$^+$], 178 (88), 136 (72).

HRMS (ESI in MeOH, H_2O, HCO_2H): *m/z* calcd for $C_{13}H_{18}NOP$ (235.26): [M + H]$^+$ 236.11988, [M + Na]$^+$ 258.10182; found: 236.11990, 258.10195.

2-*tert*-Butyl-4-methoxy-*1H*-1,3-benzazaphosphole–(2*R*)-2-*tert*-butyl-4-methoxy-2,3-dihydro-1*H*-1,3-benzazaphosphole 3-Oxide–Benzene-d_6 Cocrystallizate (3:1:2) (10)

A crystal of cocrystallizate **10** measuring 0.19 × 0.12 × 0.05 mm was mounted on a glass fiber in inert oil and transferred to the cold gas stream [100(2) K]. Data were recorded on a Bruker SMART 6000 CCDC diffractometer using Cu Kα radiation, λ = 1.54184 Å, to θ = 66.9° (96.8% complete to 66.5°). The crystal was a nonmerohedral twin by 180° rotation about *c**, associated presumably with the closeness of α and β to 90°. Absorption corrections were applied by using multiple scans, with transmissions 0.925–0.792. The structure was refined by using SHELXL-97 by full-matrix least-squares on F^2.[24] *Hydrogen atom treatment*: All hydrogen atoms at N, P3, C2 were clearly identified; NH und PH hydrogen atoms were freely refined (although the PH bond was slightly short). Methyl groups were refined as idealized rigid groups allowed to rotate but not to tip; all other hydrogen atoms were included by using a riding model starting from the calculated positions. The final *R* indices were [$I > 2\sigma(I)$] $R1$ = 0.0365, (all data) $wR2$ = 0.1018, for 696 parameters; $S(F^2)$ = 1.05, largest diff. peak and hole 0.49 and −0.30 e A^{-3}.

Crystal data:[25] Triclinic, space group $P\bar{1}$, a = 10.9825(4), b = 14.7958(5), c = 19.2873(7) Å, α = 89.739(2), β = 89.818(2), γ = 68.579(2)°, 2917.56(18) Å^3, Z = 2, D_x = 1.220 Mg/m^3, μ = 1.6 mm^{-1}, $F(000)$ = 1132.

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