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σ^2P,O-Hybrid Ligands: Synthesis of the First 4-Hydroxy-1,3-benzazaphospholes by *ortho*-Lithiation of *m*-Amidophenyl Diethyl Phosphates

Bhaskar R. Aluri,[a] Kirti Shah,[b] Neelima Gupta,[b] Olga S. Fomina,[c] Dmitry G. Yakhvarov,[c,d] Mohammed Ghalib,[a] Peter G. Jones,[e] Carola Schulzke,[f] and Joachim W. Heinicke*[a]

Dedicated to the memory of Professor Dr. Reinhard Schmutzler

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The *m*-phosphorylanilides **2** are available from anilides **1** by the Atherton–Todd reaction; the selective *ortho*-lithiation of the *o*′-methyl-protected phosphorylpivalanilide **2b** with *t*BuLi proceeded in high yield in the presence of $ClSiMe_3$. The *ortho*-lithiation is followed by rapid 1,3-migration of the PO_3Et_2 group to yield the phosphonoanilide *cis*/*trans*-**3b**. This compound mainly reacts with excess $LiAlH_4$ by reductive cyclization to form the 4-hydroxy-1*H*-1,3-benzazaphosphole **6**. The lithiation of the *o*′-unprotected phosphorylpivalanilide **2a** with LDA was unselective and led to **3a** and **4a** in low yields, whereas additional *ortho*-lithiation of the benzoyl group occurred for the lithiation of the *o*′-protected phosphonobenzanilide **2c** with *t*BuLi/LDA to give **7** in rather low yield. The reduction of crude **7** led to (benzylamino)-phenol **8** and the 4-hydroxy-1*H*-1,3-benzazaphosphole **9** as a minor product. The properties, NMR spectroscopy data, and crystal structures of **5b**, **6**, and **8** are reported.

Introduction

o-Phosphanylphenols[1,2] are well-known precursors for transition metal complexes with κ*P*-phosphanylphenol or κ^2*P*,*O*-phosphanylphenolate chelate coordination[1,3,4] for a variety of catalysts, for example, for ethylene polymerization and copolymerization with α-olefins,[4,5] ring-opening polymerization (propylene oxide, caprolactam),[6] and hydrogenation (styrene, cyclohexenes),[7] and for assemblies of ditopic ligands for rhodium-catalyzed hydroformylation.[8] However, aromatic compounds of dicoordinated phosphorus atoms (σ^2P) with OH groups in the *ortho* position and complexes thereof have been little investigated; most of them are *o*-hydroxy-,[9] *o*-hydroxymethyl-, or various hydroxyphenylphosphinine moieties.[10] Five-membered σ^2P rings with OH groups are very rare,[11] and OH-substituted 1*H*-1,3-benzazaphospholes have not yet been reported. The ring system of the latter is aromatically strongly stabilized like that of phosphinines[12] but has higher π-density at the phosphorus atom because of the conjugation of the σ^3N-donor and the dicoordinated P atom. This changes the coordination properties in the direction of π-donor bond contributions.[13] Conjugation with a hydroxy group with a +M effect should further increase the π density at the phosphorus atom and in addition offer a second OH or O^- coordination site. Thus, the synthetic access to 4-hydroxy-1,3-benzazaphospholes would provide the basis for the study of the coordination chemistry of new σ^2P,O hybrid ligands with high π density at the phosphorus atom. This prompted us to extend our longstanding investigations on a variety of 1,3-azaphospholes[14,15] to 4-hydroxy-1,3-benzazaphospholes with an OH group at the *ortho* position to the σ^2P atom.

The routes to 1,3-benzazaphospholes generally start from 2-diethylphosphonoanilines or -anilides. To access 4-hydroxybenzazaphospholes, an additional OH group at the 3-position is required. This suggests that the well-known

[a] Institut für Biochemie (Anorganische Chemie), Ernst-Moritz-Arndt-Universität Greifswald,
Felix-Hausdorff-Str. 4, 17487 Greifswald, Germany
E-mail: heinicke@uni-greifswald.de
http://www.mnf.uni-greifswald.de/institute/institut-fuer-biochemie/anorganische-chemie.html
[b] Department of Chemistry, University of Rajasthan, 302004 Jaipur, India
[c] A. E. Arbuzov Institute of Organic and Physical Chemistry, 420088 Kazan, Russian Federation
[d] Kazan Federal University, 420008 Kazan, Russian Federation
[e] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany
[f] Institut für Biochemie (Bioanorganische Chemie), Ernst-Moritz-Arndt-Universität Greifswald 17487 Greifswald, Germany

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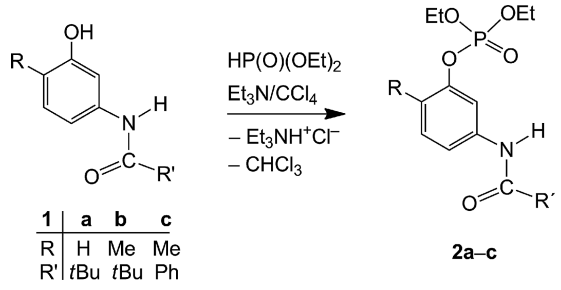
metalation–rearrangement strategy for the synthesis of (*o*-hydroxyaryl)phosphonates could be applied. In the absence of interfering functional groups, phosphonylation at the *ortho* position to an aryl OH group can be achieved in high yield by the metalation of *o*-bromoaryl diethyl phosphates with magnesium, sodium,[2b] *n*BuLi[16] or, more easily, by the directed *ortho*-lithiation of aryl diethyl phosphates with lithium diisopropylamide (LDA) in tetrahydrofuran (THF).[17] The resulting *o*-metalated aryl diethyl phosphates undergo rapid intramolecular 1,3-carbanionic C(Li) OPO_3Et_2 to C(PO_3Et_2)OLi rearrangements to form the corresponding *o*-(diethylphosphono)phenoxides. As pivalanilides similarly undergo rapid directed *ortho*-lithiation with *n*BuLi in THF at –30 to 0 °C,[18] lithiation at the common *ortho* position of the O and N substituents was expected to be preferred. A competing carbanionic 1,3-migration of the *N*-acyl group was observed only for *N*-tertiary anilides[19] and should not interfere. Therefore, we studied the applicability of the above strategy to access (2-amido-6-hydroxyphenyl)phosphonates and their conversion to 4-hydroxy-1*H*-1,3-benzazaphospholes and report here on the results and limitations.

Results and Discussion

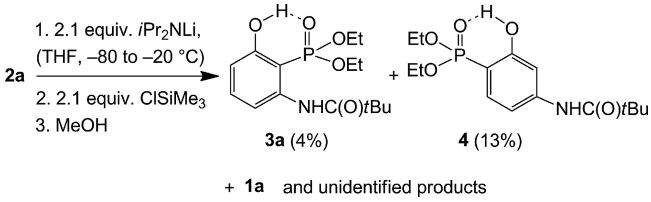
Synthesis

The starting materials, 3-hydroxy-substituted *N*-phenylpivalamide (**1a**) or *N*-tolylpivalamide (**1b**) and the analogous benzanilide **1c**, were easily accessible from the corresponding hydroxyanilines and acid chlorides in the presence of a base. The conversion into the corresponding diethyl (*m*-acylamido)phenyl phosphates **2a**–**2c** succeeded in high yields by the Atherton–Todd reaction,[20] that is, the reaction with diethyl phosphite, CCl_4, and triethylamine in THF (Scheme 1), or by direct esterification with $ClPO_3Et_2$ in the presence of triethylamine.



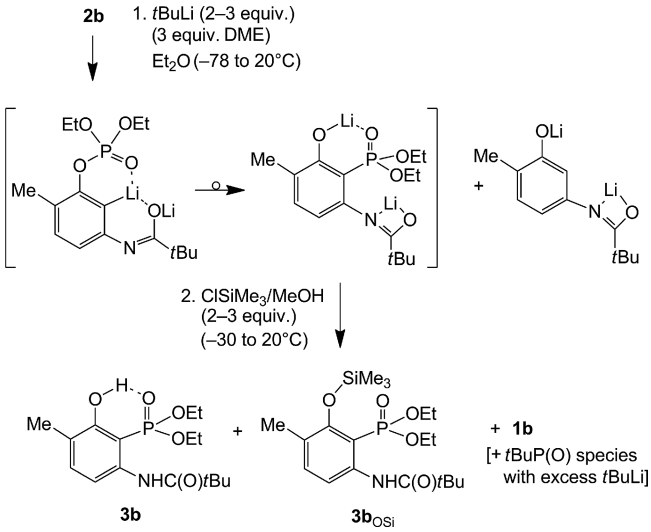
Scheme 1. Synthesis of *m*-amidoaryl diethyl phosphates **2a**–**2c**.

However, the *ortho*-lithiation/rearrangement step proved to be critical. Whereas, as noted above, LDA in THF converts common functionally unsubstituted phenyl diethyl phosphates to the respective lithium *o*-(diethylphosphono)-phenolates in high yields,[17] the reaction with **2a** was unselective and provided a mixture. ^{31}P NMR spectroscopy analysis showed sharp resonances at δ = 21.0, 18.5, and –6.5 ppm (unconsumed **2a**), as well as a broad signal in the range δ = 21–25 ppm. Separation by preparative TLC on silica gel furnished only small amounts of the desired phosphonoanilide **3a** (4%) and the regioisomer **4** (13%, Scheme 2). The formation of the latter contrasts with the selective lithiation/substitution pattern of the closely related *N*-(3-methoxyphenyl)pivalamide at the 2-position, that is, the common *ortho* position between the O and N substituents.[18]



Scheme 2. Lithiation of **2a** by LDA, followed by trapping with $ClSiMe_3$ and final *O*-desilylation.

To prevent lithiation at the competing *ortho'* position of the *ortho*-directing OPO_3Et_2 group, further experiments were performed with the methyl-protected anilidophosphate **2b**. However, all attempts at lithiation with 2–3 equiv. of LDA, *n*BuLi, or LDA/BuLi in THF (–80 to 20 °C), followed by reaction with $ClSiMe_3$ and MeOH, failed to give **3b** or gave only very small amounts. Lithiation with *t*BuLi in THF, 1,4-dioxane, or toluene likewise led to mixtures of varying compositions, whereas the use of diethyl ether as solvent gave *trans*-**3b** ($\delta^{31}P$ = 23.5 ppm) and $\mathbf{3b}_{OSi}$ ($\delta^{31}P$ = 21.3 ppm) after workup by complete or partial desilylation (for $\mathbf{3b}_{OSi}$) by methanol at room temperature (Scheme 3).



Scheme 3. Lithiation of **2b** by *t*BuLi, followed by trapping with $ClSiMe_3$ and methanolysis.

The yields of the $CDCl_3$-soluble crude products were calculated from the relative peak areas of the ^{31}P NMR signals of *trans*-**3b** and $\mathbf{3b}_{OSi}$ (Table 1). The conversion of **2b** ($\delta^{31}P$ = –5.9 ppm) and the relative content of $\mathbf{3b}/\mathbf{3b}_{OSi}$ were increased noticeably by a small excess of *t*BuLi (2.1–2.8 equiv.); however, with three or more equivalents or at larger scales (>5 g of **2b**), the formation of **3b** was disfa-

Table 1. Conversion of **2b** to **3b** under various conditions, calculated from the relative peak areas of the ^{31}P NMR signals of **2b**, **3b**, and $\mathbf{3b}_{OSi}$ in the $CDCl_3$-soluble crude products.

Amount of *t*BuLi,[a] amount of donor [mmol]; reaction mode[b]	Amount of **2b**, amount of $ClSiMe_3$ [mmol]; solvent	Conversion to **3b** and $\mathbf{3b}_{OSi}$ [%][c]	Unconverted **2b** [%];[c] major impurity (%)
4.1 (2.0 equiv.), –; A	2.05, 4.1; Et_2O	2, 22	47; δ = –5.3 (16)
11.4 (2.1 equiv.), –; A	5.4, 10.8; Et_2O	25, 17	34; δ = 61.7 (9)
30.7 (2.5 equiv.), –; A	12.3, 30.7; Et_2O	39, 30	3; δ = 63.3 (15)
10.4 (2.5 equiv.), 12.5 DME; B	4.15, 10.4; Et_2O	26, –	32; δ = 19.4 (21)
52.5 (2.5 equiv.), 63 DME, B	21.0, 52.5; Et_2O	0, 4	0; δ –1.0 (60)
8.15 (2.5 equiv.), 9.8 DME; C	3.26, 8.15; Et_2O	35, 9	9; δ = 15.9 (20)
25.5 (2.5 equiv.), 30.6 DME; C	10.2, 25.5; Et_2O	32, –	40; δ = 16.8 (10)

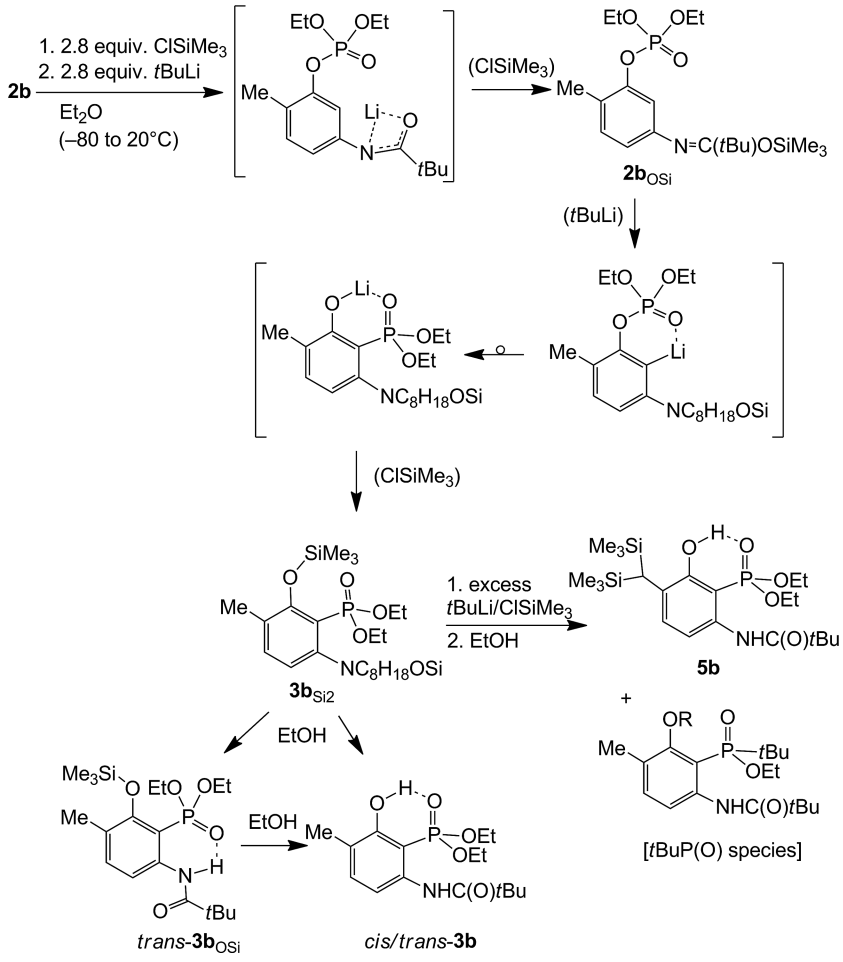
[a] Solution in pentane (1.6 M), equivalents in parentheses are relative to **2b**. [b] Reaction mode A: (normal) addition of LiR to **2b** at –80 °C, after 12–15 h at room temp. reaction with $ClSiMe_3$ (–30 to 20 °C, 4 h) and filtration; mode B: (inverse) addition of **2b** to LiR at –78 °C, after 12–15 h at room temp. reaction with $ClSiMe_3$ as in mode A; mode C: inverse lithiation as before, but trapped by MeOH/$ClSiMe_3$ solution. [c] Percentage of peak areas of ^{31}P NMR signals for the crude filtrate.

vored by increasing O_{aryl}–P bond cleavage and OEt substitution at the phosphorus atom to form **1b** and *t*BuP(O) species, respectively. Trials with some additives to promote the CH-lithiation gave rise to mixtures with a low content of **3b** for *t*BuLi/KO*t*Bu or *t*BuLi/tetramethylethylenediamine (*t*BuLi/TMEDA). Only *t*BuLi/1,2-dimethoxyethane (*t*BuLi/DME), generated in hexane before the lithiation, showed similar or slightly improved results compared to those with *t*BuLi/Et_2O in an inverse lithiation mode (the addition of **2b** in diethyl ether to the *t*BuLi/DME complex). The viscous oily *trans*-**3b** was purified by silica gel column chromatography, but losses on the column diminished the isolated yield of *trans*-**3b** to a maximum of 26%.

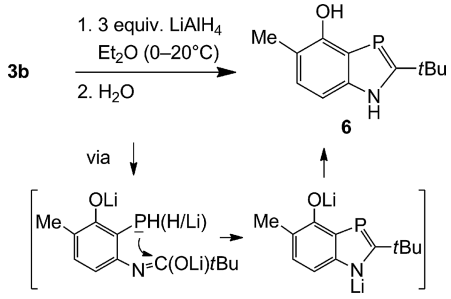
Almost complete *ortho*-lithiation, followed by instantaneous rearrangement with P–C bond formation, was achieved by the addition of excess *t*BuLi (2.8 equiv.) at –80 °C to an ethereal solution of **2b** and an excess of $ClSiMe_3$ (2.8 equiv.), followed by slow warming. The reaction with a smaller excess of *t*BuLi (2.5 equiv.) at –60 °C was less suitable and led to an increased formation of aryl–*t*BuP(O)(OEt) side products at the expense of the conversion of **2b**. The primary silyl compounds, that is, the highly viscous crude product $\mathbf{3b}_{Si2}$ and others, were somewhat sensitive to moisture, alcohols, or active OH groups on silica gel and were, thus, unsuitable for separation by chromatography. Therefore, the crude mixture was heated at reflux with EtOH to yield mainly *cis*- and *trans*-**3b** (56 and 28% by ^{13}C NMR integration) along with small amounts of the partly desilylated $\mathbf{3b}_{OSi}$, **5b**, and aryl–*t*BuP(O)(OEt) species. After evaporation of the solvent and volatile products under vacuum, the semisolid residue was extracted with pentane/diethyl ether (20:1) to leave the sparingly soluble *cis*-**3b** in 49% yield as a high-melting powder. It is readily soluble in $CDCl_3$ and did not isomerize in dry $CDCl_3$ at room temperature over 3 d because of its sufficiently high barrier for *cis*/*trans* isomerization.[21] However, in the presence of moisture, slow conversion to *trans*-**3b** and small amounts of other species with ^{31}P NMR signals at δ = 16.0 and 17.2 ppm was observed. In the pentane extract, *trans*-**3b**, $\mathbf{3b}_{OSi}$, **5b**, and two aryl–*t*BuP(O)(OEt) compounds were enriched. Concentration under vacuum led to crystals of **5b**, which could be partly separated and were suitable for structure determination, whereas good solubility in pentane prevented their quantitative separation.

The improved *ortho*-lithiation/P–C coupling in the presence of $ClSiMe_3$ is attributed to the very slow reaction of *t*BuLi with $ClSiMe_3$ at low temperature; whereas the silylation is sufficiently fast for the reactive lithium intermediates that interfere with the *ortho*-CH-lithiation. Thus, the lithiation of **2b** with 1 equiv. of *t*BuLi in the presence of $ClSiMe_3$ at –60 °C led to $\mathbf{2b}_{OSi}$ as the main product (88%) and proves that primary lithiation occurs at the NH function. A lack of color change to orange-red, as reported for lithium *N*-arylimidates,[19] hints at rapid trapping by $ClSiMe_3$. Therefore, it can be assumed that the formation of $\mathbf{2b}_{OSi}$ during the lithiation of **2b** with excess *t*BuLi in the presence of excess $ClSiMe_3$ in combination with the phosphono group allows efficient *ortho*-lithiation, followed by immediate intramolecular migration of the diethylphosphono group from the oxygen atom to the carbon atom. An excess of *t*BuLi is required for complete conversion of **2b**, but it also causes side reactions such as CH-lithiation at the 2-methyl group and substitution of an OEt group at the phosphorus atom, which lead to small amounts of bis(trimethylsilyl)methyl and aryl–*t*BuP(O)$(OEt)_2$ species, respectively (Scheme 4).

The conversion of the phosphonoanilides **3b** to 4-hydroxy-1,3-benzazaphosphole (**6**) was accomplished by reductive cyclization with excess lithium aluminum hydride (3.0 equiv.) and hydrolytic workup. The use of pure *trans*-**3b** and final purification by crystallization from THF/hexane gave **6** in 60% yield (Scheme 5). The reduction of *cis*-**3b** with excess $LiAlH_4$ (3.5 equiv.) under similar conditions proved less suitable. After hydrolysis, a mixture of *trans*-**3b**, **6**, and a primary phosphanylaniline was detected (^{31}P NMR peak area ratio 41:32:27). Even more side products were observed for the direct reduction of the crude mixture formed by *ortho*-lithiation in the presence of excess $ClSiMe_3$. In this case, pure **6** was isolated in low yield (19% relative to **2b**) by column chromatography and extraction of N-basic impurities with cold 10% aqueous sulfuric acid.



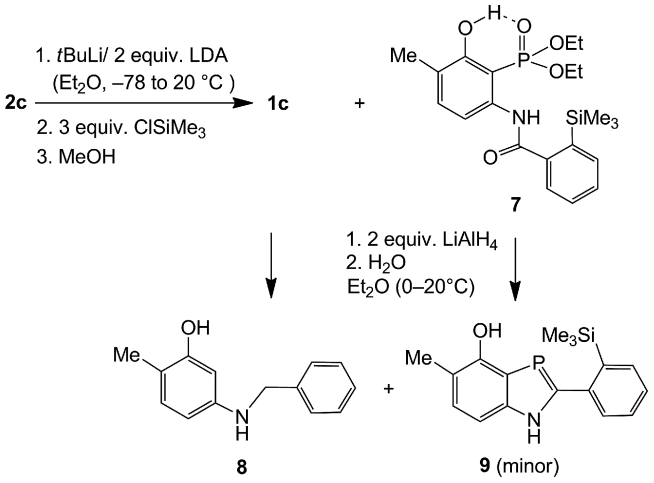
Scheme 4. Products formed by the lithiation of **2b** in the presence of $ClSiMe_3$ and subsequent alcoholysis (intermediates supposed).



Scheme 5. Reductive cyclization of **3b** to **6**.

The reaction of **3b** to **6** proceeds by primary reduction of the phosphono group and intramolecular nucleophilic addition of the resulting PH_2 or PHLi group at the lithiated amide (imidate) group, as discussed earlier.[22] N-Basic phosphane side products were separated by extraction with dilute aqueous sulfuric acid. This is possible, because **6** is not basic and is stable to the addition of water at the P=C bond, even in cold diluted aqueous acids. The N lone pair is involved in the aromatic π system of **6**[12] and stabilizes the P=C bond. Crystalline **6** is not markedly attacked by air on contact for a few minutes, whereas in solution the compound is rapidly oxidized.

Attempts to *ortho*-lithiate the phosphonobenzanilide **2c** with LDA or *n*BuLi failed similarly to the attempt reported above for **2b**. A well-defined product was obtained by reaction with excess *t*BuLi/LDA, generated from *t*BuLi and iPr_2NH in cold diethyl ether before addition to the ethereal solution of **2c** (–78 °C). The resulting lithium species was quenched with $ClSiMe_3$ to provide the *o*-trimethylsilylated phosphonobenzanilide **7**, which indicates that a second competing *ortho*-lithiation occurs at the benzimidate structural unit (Scheme 6). Like that of *trans*-**3b** generated in the absence of $ClSiMe_3$, the yield of **7** was low (28% after purification by column chromatography), and substantial amounts of the P–O bond-cleavage product **1c** formed. The direct reduction of the crude product led to a mixture; after separation of 5-benzyl-2-methylphenol (**8**, the reduction product of **1c**), a minor amount of 4-hydroxy-2-[(*o*-trimethylsilyl)phenyl]benzazaphosphole (**9**) was detected by its characteristic NMR spectroscopic data. Attempts to purify **9** by column chromatography were unsuccessful.



Scheme 6. Formation of **7** by double *ortho*-lithiation of **2c** and of **8** and **9** by reduction of the crude product mixture.

Structural Aspects

The structure elucidation of the new compounds is based on conclusive multinuclear solution NMR spectroscopic data, supplemented by satisfactory elemental analyses or HRMS data (for purity, see NMR spectra, Figures S1–S34 in the Supporting Information) and by crystal structure analyses for **5b**, **6** and **8**. The ^{1}H and ^{13}C nuclei of the aromatic rings of the new compounds display the expected NMR signal splittings with $^{3}J_{H,H}$ and typical $^{4}J_{P,H}$ (5–6 Hz) and $^{1}J_{P,C}$ (170–180 Hz) coupling constants and chemical shifts in accordance with values estimated from those of related compounds[14,15] and substituent effects. Compared to those of phosphinines,[9,10,23] the ^{31}P NMR resonances of benzazaphospholes are dramatically shifted to low frequency by the π donation of the $\sigma^{3}N$ atom in conjugation to $\sigma^{2}P$; the resonance is further shifted in **6** by $\Delta\delta$ = –12 ppm in comparison with that of 2-*tert*-butyl-5-methyl-1*H*-1,3-benzazaphosphole.[22] This is attributed to the +M effect of the OH group rather than to steric shielding, as the steric effects of Me, *t*Bu, or Ph groups versus an H atom at the 2-position to the phosphorus atom are much smaller than the electronic effects of –M or +M substituents (COOH or NHPh) at the same position.[14,15] Thus, **6** is an example of a functionally substituted, π-electron-rich $\sigma^{2}P$ heterocycle.

The ^{31}P NMR chemical shifts of the phosphorylanilides **2a**–**2c** and the phosphonylanilides **3a**, **3b**, **4a**, and **7** display characteristic values in the range δ = –5.9 to –6.3 ppm and δ = 22.7 to 24.0 ppm, respectively. In proton-acceptor solvents such as [D_6]dimethyl sulfoxide ([D_6]DMSO) or [D_7]-*N*,*N*-dimethylformamide ([D_7]DMF), the ^{31}P NMR resonance of *cis*-**3b** is shifted to higher frequency (δ = 28, 29 ppm). The aryl–*t*BuP(O)(OEt) side products are indicated by ^{31}P NMR resonances in the range δ = 50–63 ppm and by *t*Bu(P) and *i*-C(P) doublets in the ^{13}C NMR spectra with $^{1}J_{P,C}$ = 99–104 Hz, both characteristic of aryl–*t*BuP(O)X compounds.[24] The proton signals of the aryl CH groups between the phosphoryl and amido groups in **2a**–**2c** (δ = 7.48–7.86 ppm) or at *ortho* position to the amido group of **3a**, *trans*-**3b**, **5b**, **7**, and particularly $\mathbf{3b}_{OSi}$ ($\delta_{5\text{-H}}$ = 7.59–7.74, 8.25 ppm) appear at low field because of the anisotropic influence of the C=O group,[21] which is turned towards these protons by an efficient intramolecular N–H···O=P hydrogen bond. In *cis*-**3b**, the opposite orientation of the C=O group is probable, as indicated by the rather low-frequency chemical shift of 5-H (δ = 7.10 ppm). Much stronger low-frequency shifts are observed for the protons at the *ortho* positions of the silylimidate $\mathbf{2b}_{OSi}$ (δ = 6.52, 6.77 ppm). The silylimidate nature is further indicated by the C=N ^{13}C NMR resonance[25] at δ = 163.97 ppm, which is markedly different from the C=O signal of **2b** at δ = 176.69 ppm. The acidic NH···O=P proton of $\mathbf{3b}_{OSi}$ is observed at δ_{NH} = 11.48 ppm (cf. δ = 9.63–11.93 ppm for related compounds),[15c] whereas the NH proton signals of the *o*-hydroxyphosphonoanilides **3a**, **3b**, **4a**, and **7** appear at δ = 8.15–8.45 ppm. In these compounds, the phosphono group favors an intramolecular hydrogen bond with the OH proton (δ = 10.58–11.67 ppm). For **6** in solution, an intramolecular O–H···P hydrogen bond was not detectable, in accordance with the low basicity of the dicoordinated neutral phosphorus atom. The broad signals for the OH group at δ = 4.96 ppm and for the NH group at δ = 8.40 ppm (cf. ref.[14,15]) suggest rather weak intermolecular hydrogen bonds.

Information on the solid-state structures of **5b**, **6**, and **8** was provided by single-crystal X-ray diffraction. For **5b** (Figure 1), the conformation of the phosphono group is controlled by an intramolecular O–H···O=P hydrogen bond. The π planes of the amide group and the benzene ring are twisted along the N1–C6 bond by 98°. This is predominantly caused by N1–H···O2 intermolecular hydrogen bonding of the amide moiety and further stabilized by intermolecular hydrogen bonding between C-9 of the *t*Bu group and O-2; that is, O-2 of one molecule is hydrogen-bonded both to C-9–H and to N-1–H of a second molecule. The bond lengths and angles within the molecule are in the usual ranges.

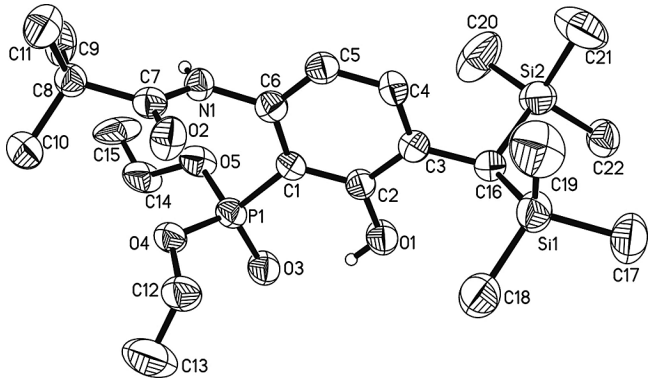


Figure 1. Molecular crystal structure of **5b**. Ellipsoids represent 50% probability levels; protons, except those bound to N and O, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.775(6), P1–O3 1.480(5), C6–N1 1.428(8), N1–C7 1.342(8), C7–O2 1.233(7), C2–O1 1.362(7); C6–N1–C7 122.5(5), O3–P1–O5 116.0(3), O4–P1–O5 102.6(2), O3–P1–C1 110.7(3).

The crystal structure analysis of the deuteriobenzene solvate of **6** (Figure 2) reveals a planar ring system and bond lengths and angles similar to those of 2-*tert*-butyl-1*H*-1,3-benzazaphosphole,[22] and no noticeable changes are induced by the 4-OH group. The C-4–O bond length is in the typical range for the C–O bonds of phenols. The OH group forms intermolecular N–H···O hydrogen bonds and weak O–H···P contacts, as illustrated in the packing (Figure 3).

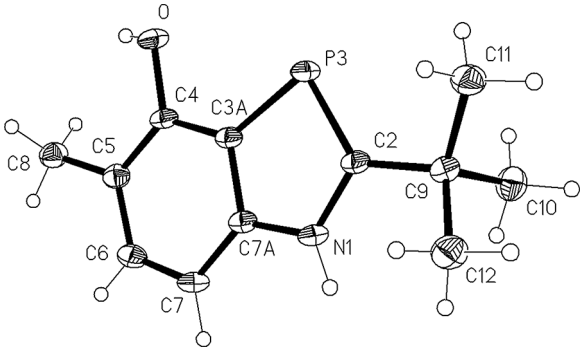


Figure 2. Molecular crystal structure of **6**. Ellipsoids represent 50% probability levels. Selected bond lengths [Å] and angles [°]: P3–C2 1.7397(11), P3–C3A 1.7878(11), C2–N1 1.3629(14), N1–C7A 1.3780(14), C3A–C7A 1.4071(15), C4–O 1.3859(13); N1–C2–P3 112.86(8), C2–P3–C(3A) 89.02(5), P3–C2–C9 128.10(8), N1–C2–C9 118.86(9).

The crystal structure analysis of **8** (Figure 4) confirmed the absence of a trimethylsilyl group at the phenyl ring and suggests that the compound originates from the reduction of the decomposition product **1c**, which was detected for the reaction of **2c** with *t*BuLi/LDA. The formation during the reduction of the phosphonoanilide **7** by cleavage of the P–C bond would require additional cleavage of the Si–C bond. The structure data are typical for a benzylaniline and are consistent with sp^2 hybridization of the nitrogen atom; which, in combination with the approximately coplanar arrangement of the N–C17 bond and the plane of the phenol ring [dihedral angles C6–C1–N–C17 169.36(9), C2–C1–N–C17 13.00(14)°], allows conjugation with the phenol π system. In contrast, the phenyl group is nearly perpendicular to the C17–N bond [C12–C11–C17–N 81.80(13)°, C16–C11–C17–N 100.81(12)°]. The packing of the molecules (see Supporting Information) is controlled by intermolecular N–H···O and O–H···N hydrogen bonds.

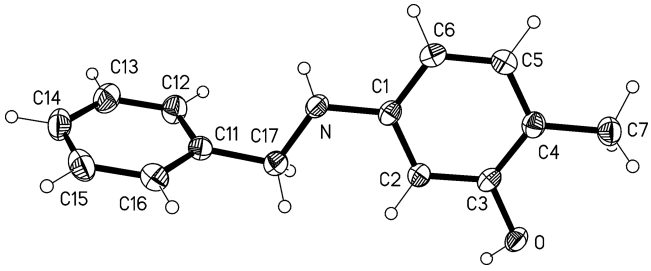


Figure 4. Molecular crystal structure of **8**. Ellipsoids represent 50% probability levels. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.3937(14), C(1)–N 1.4258(13), C(17)–N 1.4780(14); C(2)–C(1)–N 121.54(9), C(1)–N–C(17) 116.52(8).

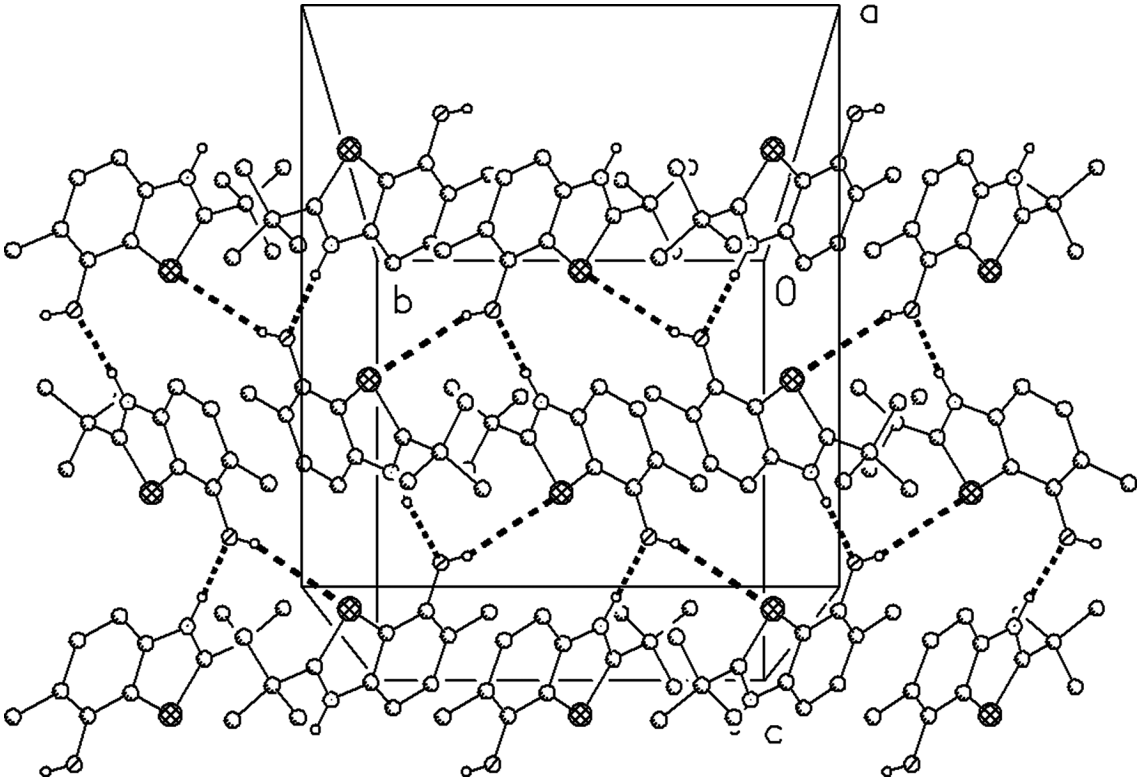


Figure 3. Crystal packing of **6**. Dashed lines indicate hydrogen bonds.

Conclusions

The lithiation of *N*-secondary *m*-phosphorylpivalanilides at the common *ortho* position (between the O and N substituents), followed by 1,3-O,C migration of the PO_3Et_2 group as is typical for *o*-metalated aryl phosphates,[17] is strongly disfavored compared to the well-established directed *ortho*-lithiations of aryl diethyl phosphates or *N*-secondary pivalanilides without interfering functional groups. This is shown by the very low yields of **3a** and **3b** and the low yield of **7** for the classic lithiation strategy with LDA; the latter case is accompanied by additional *ortho*-lithiation of the benzoic acid residue. The *ortho*-lithiation is slightly improved with *t*BuLi in diethyl ether and is much more efficient with *t*BuLi in the presence of $ClSiMe_3$. With excess *t*BuLi (2.8 equiv. relative to **2b**), the degree of phosphonylation at the common *ortho* position reached 84%. Owing to the competing partial lithiation/silylation of the *o′*-methyl group (a new type of aryl phosphate directed lithiation) and *tert*-butylation of the diethylphosphono group by the excess *t*BuLi that is necessary to achieve complete conversion of **2b**, some side products formed. Concerning the strong effect of $ClSiMe_3$, we suppose that the polar Li species that hinder the *ortho*-lithiation, for example, by interactions with the O=P donor group, are trapped by silylation, and this then allows the phosphate-directed *ortho*-lithiation, followed by the well-known rapid 1,3-intramolecular shift of the PO_3Et_2 group. It still has to be investigated whether a primarily formed silylimidate group additionally supports the *ortho*-lithiation at the common *ortho* position of *m*-phosphorylarylsilylimidates and allows the selective lithiation even of **2a**, **2c**, and related compounds in the presence of $ClSiMe_3$.

The reductive cyclization of the *o*-hydroxyphosphonoanilide **3b** to form the first 4-hydroxy-1*H*-1,3-benzazaphosphole, **6**, suggests that this synthetic route is also suitable for related 2-*tert*-butyl-4-hydroxy-substituted benzazaphospholes. The limitations for the synthesis of 2-aryl-substituted 4-hydroxybenzazaphospholes by this route are the additional *ortho*-lithiation of the benzoic acid residue, which was observed for lithiation with *t*BuLi/LDA, and the low yields of **9** after reduction. The application of the *t*BuLi/$ClSiMe_3$ lithiation strategy, which was developed in the final stage of these studies, might also improve the synthesis of 2-aryl derivatives. The knowledge of a synthetic access to 4-hydroxy-1,3-benzazaphospholes, represented by **6**, paves the way for future studies of the coordination behavior of these new π-electron-rich σ^2P,O hybrid ligands. Although solutions prepared from **6** and $Ni(COD)_2$ (COD = cyclooctadiene) were unstable and induced only low catalytic conversion of ethylene to low-molecular-weight oligomers in batch-screening tests,[2d] there is a good chance that benzazaphosphole hybrid complexes will be obtained with d^{10} coinage metal compounds, which form isolable complexes with monodentate benzazaphosphole ligands.[13]

Experimental Section

General: All operations were performed under nitrogen by Schlenk techniques. The solvents CCl_4 and triethylamine were dried by standard procedures and freshly distilled before use. Other chemicals were used as purchased. NMR spectra were recorded with an Avance II 300 (Bruker) multinuclear FT-NMR spectrometer at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Chemical shifts are given in ppm and are referenced to $SiMe_4$ or solvent signals and calibrated with this standard for ^{1}H and ^{13}C NMR spectra and with H_3PO_4 (85%) for ^{31}P NMR spectra. Coupling constants refer to $J_{H,H}$ in ^{1}H NMR spectra and $J_{P,C}$ in ^{13}C NMR spectra unless indicated otherwise. The assignment numbers follow the nomenclature numbering scheme. For phenyl groups, indication of position by *i*/*o*/*m*/*p* is used. The relative peak areas of ^{31}P NMR signals (measured with AQ = 0.65 s, D1 = 2.0 s) are given in $\%\Sigma_{integral}$ and may deviate from the quantitative ratios. Low-resolution mass spectra were recorded with an AMD40 (Maurer) instrument, and HR mass (ESI) spectra were recorded in Göttingen with an APEX IV (Bruker Daltonics) 7 T Fourier transform ion cyclotron resonance mass spectrometer or with a micrOTOF instrument. Melting points were determined with a Sanyo Gallenkamp melting point apparatus, and elemental analysis was performed with a CHNS-932 analyzer from LECO under standard conditions.

***N*-(3-Hydroxyphenyl)-2,2-dimethylpropionamide (1a) and *N*-(3-Hydroxy-4-methylphenyl)-2,2-dimethylpropionamide (1b):** Compound **1a** was prepared according to a literature procedure.[26] The synthesis of compound **1b** was performed analogously.[27] The ^{13}C NMR spectra of these starting materials are depicted in the Supporting Information.

***N*-(3-Hydroxy-4-methylphenyl)benzamide (1c):** Benzoyl chloride (4.98 mL, 43 mmol) was added dropwise at 0 °C to a mixture of 5-amino-2-methylphenol (5.05 g, 41 mmol), $NaHCO_3$ (84.0 g, 123 mmol), ethyl acetate (160 mL), and water (180 mL). The mixture was stirred for 2 h, and the organic phase was separated and washed with 1 N HCl, followed by water and brine. The resulting solution was dried with Na_2SO_4 and concentrated at reduced pressure to give 7.94 g (91%) of an off-white solid, m.p. 206–207 °C. The NMR spectra in [D$_6$]acetone display *cis*/*trans* isomers; the less abundant isomer does not have a hydrogen bond, and the other isomer does have a hydrogen bond. ^{1}H NMR ([D$_6$]acetone): δ = 2.17 (s, 3 H, 2-CH_3), 2.88 (s, OH, H_2O of solvent), 2.91 (s, OH), 7.02 (d, ^3J = 8.1 Hz, 1 H, 5-H), 7.10 (dd, ^3J = 8.1 Hz, ^4J = 2.1 Hz, 1 H, 6-H), 7.42–7.58 (m, 3 H, 2 *m*-H, *p*-H), 7.56 (superimposed d, ^4J = 2.0 Hz, 1 H, 2-H), 7.95 (m, $^3J \approx$ 6.8 Hz, ^4J = 1.5 Hz, 2 H, *o*-H), 8.29 (s, 0.25 H, NH), 9.36 (br. s, half-width = 15 Hz, 0.75 H, NH···O) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 16.4 (2-CH_3), 108.42, 108.51, 112.67, 112.76 (C-2, C-4), 121.11 (br., *cis*- and *trans*-C_q-2 superimposed), 128.90, 129.86, 131.9, 132.8 (C-*o*,*m*,*p*, C-3), 137.1 (br., *cis*- and *trans*-C_q-5), 139.57, 139.66 (C_q-*i*), 156.73, 156.75 (C-1), 166.79, 166.86 (CO) ppm. MS (EI, 70 eV, 340 °C): *m*/*z* (%) = 227 (36) [M]$^+$, 105 (100), 77 (49), 51 (12). $C_{14}H_{13}NO_2$ (227.26): calcd. C 73.99, H 5.77, N 6.16; found C 73.96, H 5.79, N 6.07.

3-(2,2-Dimethylpropanamido)phenyl Diethyl Phosphate (2a): Diethyl phosphite (0.36 mL, 2.85 mmol) was added to a mixture of **1a** (0.5 g, 2.59 mmol) and Et_3N (1.08 mL, 7.76 mmol) in CCl_4 (5 mL) and THF (5 mL). The mixture was heated to 50 °C for 24 h and cooled to room temperature, and the precipitated $Et_3NH^+Cl^-$ was removed by filtration and washed thoroughly with ethyl acetate. The combined filtrates were concentrated and purified by flash column chromatography (30% ethyl acetate/hexane) to give a pale yellow oil (780 mg, 91%). ^{1}H NMR ($CDCl_3$): δ = 1.29 (s, 9 H, CMe_3), 1.35 (td, ^3J = 7.1 Hz, ^4J = 1.0 Hz, 6 H, CH_3), 4.21 (quintd, ^3J = $^3J_{PH}$ = 7.1 Hz, *J* = 1.0 Hz, 4 H, OCH_2), 6.93 (d unresolved dt, ^3J

= 8.2 Hz, $^4J_{P,H}$ = 2.3, $^4J + {}^{4'}J \approx$ 2.3 Hz, 1 H, 6-H), 7.20 (t, ^3J = 8.2 Hz, 1 H, 5-H), 7.35 (d unresolved dt, ^3J = 8.2 Hz, ^4J = 1.8 Hz, ^4J, $^6J_{P,H} \approx$ 1.5 Hz, 1 H, 4-H), 7.58 (br., unresolved t with small $^4J \approx {}^4J_{P,H}$, 1 H, 2-H), 7.90 (br. s, half-width = 5 Hz, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.87 (d, ^3J = 6.7 Hz, CH_3), 27.29 (C*Me*$_3$), 39.45 (C_qMe$_3$), 62.48 (d, ^2J = 6.2 Hz, OCH_2), 111.88 (d, ^3J = 5.5 Hz, C-2), 114.93 (d, ^3J = 4.4 Hz, C-6), 116.46 (s, C-4), 129.42 (s, C-5), 139.59 (C_q-3), 150.63 (d, ^2J = 6.9 Hz, C_q-1), 176.84 (CO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –6.3 ppm. $C_{15}H_{24}NO_5P$ (329.33). MS (EI, 70 eV, 150 °C): *m*/*z* (%) = 330 (12), 329 (62) $[M]^+$, 246 (12), 245 (99.6), 189 (34), 119 (40), 57 (100).

5-(2,2-Dimethylpropanamido)-2-methylphenyl Diethyl Phosphate (2b): Diethyl phosphite (13.6 mL, 106 mmol) was added to a mixture of **1b** (20.0 g, 96.5 mmol) and Et_3N (40.3 mL, 289 mmol) in CCl_4 (200 mL). This reaction mixture was heated to reflux for 4 h and then warmed to room temperature. The solids were removed by filtration and washed thoroughly with ethyl acetate. The filtrate was concentrated and purified by column chromatography with 30% ethyl acetate/hexane to elute impurities and unconverted **1b** and with 35% ethyl acetate/hexane to elute the product. The removal of the solvent under vacuum gave a highly viscous colorless substance (22.9 g, 69%). ^1H NMR ($CDCl_3$): δ = 1.28 (s, 9 H, CMe_3), 1.35 (td, ^3J = 7.1 Hz, ^4J = 1.0 Hz, 6 H, CH_3), 2.25 (s, 3 H, CH_3), 4.17–4.27 (m, 4 H, OCH_2), 7.09 (d, ^3J = 8.3 Hz, 1 H, 3-H), 7.38 (dd, ^3J = 8.3 Hz, ^4J = 1.7 Hz, 1 H, 4-H), 7.48 (br., unresolved t, 1 H, 6-H), 7.62 (br. s, half-width = 5 Hz, NH) ppm. $^{13}C\{^1H\}$ NMR (DEPT, $CDCl_3$): δ = 15.84 (s, CH_3), 16.10 (d, ^3J = 6.7 Hz, CH_3), 27.55 (CMe_3), 39.55 (C_q–CMe_3), 64.67 (d, ^2J = 6.2 Hz, OCH_2), 111.94 (d, ^3J = 2.3 Hz, C-6), 116.89 (d, ^4J = 0.9 Hz, C-4), 124.62 (d, ^3J = 6.4 Hz, C_q-2), 131.17 (C-3), 137.16 (d, ^4J = 1.5 Hz, C_q-5), 148.92 (d, ^2J = 7.2 Hz, C_q-1), 176.69 (CO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –5.9 ppm. MS (EI, 70 eV, 100 °C): *m*/*z* (%) = 344 (8) $[M]^+$, 343 (46), 259 (78), 231 (24), 230 (11), 122 (18), 105 (75), 57 (100). HRMS (ESI, MeOH/H_2O/HCOOH): calcd. for $C_{16}H_{26}NO_5P$ $[M + H]^+$ 344.16214; found 344.16220; calcd. for $[M + Na]^+$ 366.14408; found 366.14409.

5-Benzamido-2-methylphenyl Diethyl Phosphate (2c): Diethyl phosphite (4.22 mL, 33 mmol) was added to a mixture of **1c** (5.0 g, 22 mmol) and Et_3N (9.19 mL, 66 mmol) in CCl_4 (150 mL) and THF (30 mL). The mixture was heated to reflux for 4 h, and workup as described for **2a** gave **2c** as a white solid (5.5 g, 70%); m.p. 124–125 °C. ^1H NMR ($CDCl_3$): δ = 1.35 (td, ^3J = 7.1 Hz, $^4J_{P,H}$ = 1.1 Hz, 6 H, CH_3), 2.20 (s, 3 H, 2-CH_3), 4.19 (dquint, $^3J_{P,H} \approx {}^3J$ = 7.1 Hz, 4 H, OCH_2), 7.11 (d, ^3J = 8.2 Hz, 1 H, 3-H), 7.38–7.53 (m, 4 H, 2 *m*-H, *p*-H, 4-H), 7.63 (br., unresolved t, 1 H, 6-H), 7.86 (m, $^3J \approx$ 8.0 Hz, ^4J = 1.3 Hz, 2 H, *o*-H), 8.43 (br. s, half-width = 4.7 Hz, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.82 (s, 2-CH_3), 16.08 (d, ^3J = 6.7 Hz, OCH_2CH_3), 64.69 (d, ^2J = 6.5 Hz, OCH_2), 111.94 (d, ^3J = 2.3 Hz, C-6), 116.9 (s, C-4), 124.8 (d, ^3J = 6.6 Hz, C_q-2), 127.28, 128.55 (2s, C-*o*,*m*), 131.28 (s, C-3), 131.6 (s, C-*p*), 134.97 (s, C_q-*i*), 137.23 (s, C_q-5), 148.9 (d, ^2J = 6.8 Hz, C_q-1), 165.9 (CO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –6.3 ppm. MS (EI, 70 eV, r.t.): *m*/*z* (%) = 364 (7) $[M]^+$, 149 (7), 105 (21), 58 (100). HRMS (ESI, MeOH/NaOAc): calcd. for $[M + Na]^+$ 386.11278; found 386.11287. $C_{18}H_{22}NO_5P$ (363.34): calcd. C 59.50, H 6.10; found C 59.12, H 6.06.

Diethyl *trans*-[6-(2,2-Dimethylpropanamido)-2-hydroxy-3-methylphenyl]phosphonate (*trans*-3b): A solution of *t*BuLi in pentane (1.80 mL, 1.7 M, 3.06 mmol) was added dropwise to a solution of **2b** (0.50 g, 1.46 mmol) in diethyl ether (5 mL) at –80 °C. A yellow precipitate formed after a few minutes. Stirring was continued as the mixture warmed to room temperature overnight. Then, excess Me_3SiCl (0.39 mL, 3.06 mmol) was added at –30 °C. After 8 h at room temperature, the precipitate was removed by filtration and washed with diethyl ether. The pale yellow filtrate was concentrated under reduced pressure and separated by silica gel column chromatography. Elution with 15% ethyl acetate/hexane gave *trans*-**3b** as a colorless oil (115 mg, 26%). ^1H NMR ($CDCl_3$): δ = 1.31 (s, 9 H, CMe_3), 1.33 (t, ^3J = 7.1 Hz, 6 H, CH_3), 2.20 (s, 3 H, CH_3), 4.00–4.26 (m, 4 H, OCH_2), 7.29 (d, ^3J = 8.3 Hz, 1 H, 4-H), 7.59 (dd, ^3J = 8.2 Hz, $^4J_{P,H}$ = 5.6 Hz, 1 H, 5-H), 8.12 (br. s, half-width = 11 Hz, NH), 10.80 (s, OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.72 (d, ^4J = 1.7 Hz, CH_3), 15.98 (d, ^3J = 6.7 Hz, CH_3), 27.26 (s, C*Me*$_3$), 39.61 (s, C_qMe$_3$), 63.00 (d, ^2J = 4.4 Hz, OCH_2), 98.08 (d, ^1J = 171.3 Hz, C_q-1), 113.60 (d, ^3J = 10.3 Hz, C-5), 122.25 (d, ^3J = 11.5 Hz, C_q-3), 136.07 (d, ^4J = 1.7 Hz, C-4), 137.60 (d, ^2J = 1.6 Hz, C_q-6), 160.58 (d, ^2J = 5.4 Hz, C_q-2), 176.27 (CO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 23.9 ppm. MS (EI, 70 eV, 80 °C): *m*/*z* (%) = 343 (14) $[M]^+$, 286 (15), 259 (11), 185 (13), 148 (17), 147 (100), 73 (24), 57 (70). HRMS (ESI, MeOH/H_2O, HCOOH): calcd. for $C_{16}H_{27}NO_5P$ $[M + H]^+$ 344.16214; found 344.16220; calcd. for $[M + Na]^+$ 366.14408; found 366.14397.

Diethyl *cis*/*trans*-[6-(2,2-Dimethylpropanamido)-2-hydroxy-3-methylphenyl]phosphonate (*cis*-3b, *trans*-3b) and the Detection of 5b and *t*BuP(O)OEt-Substituted Side Products: *t*BuLi in pentane (9.6 mL, 1.9 M, 18.2 mmol) was added dropwise to a solution of **2b** (2.24 g, 6.52 mmol) and $ClSiMe_3$ (2.3 mL, 18.2 mmol) in diethyl ether (20 mL) at –85 °C. The resulting orange-red solution was warmed slowly to room temperature (still immersed in the cooling medium). At –30 to –20 °C, a color change to yellow and the formation of a white precipitate was observed. After the solution had been stirred overnight, the fine precipitate (LiCl) was separated by centrifugation, and the solvent was removed under vacuum to give a pale yellow, highly viscous crude product mixture (3.32 g). This was desilylated by heating to reflux in dry EtOH (10 mL) for 15 h. The solvent was removed under vacuum, and ^{31}P NMR monitoring of the highly viscous substance in $CDCl_3$ showed an intense signal at δ = 23.8–24.2 ppm (relative peak area 84%, *cis*/*trans*-**3b**) and small signals at δ = 20.1 (6%, $\mathbf{3b}_{OSi}$), 59.7 (4%, **A**), and 63.1 ppm (7%, **B**). The ratio of *cis*-**3b**/*trans*-**3b** was roughly 2:1 on the basis of the ratio of ^{13}C NMR signals and corresponded to crude yields of 56 and 28%. The mixture was treated with pentane/Et_2O (20:1 mL), filtered, washed with pentane (20 mL), and dried to furnish *cis*-**3b** as a beige powder (1.22 g, m.p. 220–222 °C), which still contained ca. 10% of *trans*-**3b** (corrected yield of *cis*-**3b** 49%). *cis*-**3b**: ^1H NMR ($CDCl_3$): δ = 0.91 (br. t, ^3J = 7 Hz, 3 H, CH_3), 1.22–1.34 (superimposed m, 3 H, Me), 1.23 (s, 9 H, CMe_3), 2.22 (s, 3 H, CH_3), 3.10–3.45 (m, 2 H, OCH_AH_B), 4.03 (br. t, ^3J = 6.4 Hz, 2 H, OCH_2), 4.0–4.3 (superimposed br. s, 1 H, OH), 7.08–7.17 (m, 2 H, 4-H, 5-H), 8.11 (br. s, half-width 4 Hz, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.90, 16.13 (2 superimposed d, $^3J \approx$ 8 Hz, CH_3), 18.26 (s, CH_3), 27.42 (CMe_3), 39.55 (*C*Me_3), 61.94, 62.01 (2 superimposed d, $^2J \approx$ 6 Hz, OCH_2), 101.63 (d, ^1J = 177.8 Hz, C_q-1), 110.51 (d, ^3J = 10.6 Hz, C-5), 126.44 (d, ^3J = 10.6 Hz, C_q-3), 134.58 (br. s, C-4), 138.57 (br. d, ^2J = 5.3 Hz, C_q-6), 170.73 (br., C_q-2), 175.97 (CO) ppm. $^{31}P\{^1H\}$ NMR: δ = 24.2 ($CDCl_3$), 28.0 ([D_6]DMSO), 29.0 (moist [D_7]DMF) ppm. HRMS (ESI): calcd. for $C_{16}H_{25}NO_5P$ $[M – H]^-$ 342.1476; found 342.1480; calcd. for $[M – H – C_2H_4]^-$ 314.1152; found 342.1161. $C_{16}H_{26}NO_5P$ (343.36): calcd. C 55.97, H 7.63, N 4.08; found C 55.43, H 7.21, N 4.24.

Removal of the solvent from the filtrate left a pale yellow, viscous oil (1.09 g) containing various components: ^{31}P NMR ($CDCl_3$): δ = 23.5 (27%, *trans*-**3b**), 24.3 (24%, **5b**), 59.9 (10%, **A**), 63.2 (15%,

Table 2. Crystal data and structure refinement for **5b**, **6**, and **8**.

Compound	**5b**	**6**·C_6D_6	**8**
Empirical formula	$C_{22}H_{42}NO_5PSi_2$	$C_{18}H_{16}D_6NOP$	$C_{14}H_{15}NO$
Formula weight	487.72	305.78	213.27
Temperature [K]	170(2)	133(2)	103(2)
Wavelength [Å]	0.71073	0.71073	1.54184
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/c$
a [Å]	13.802(3)	26.048(2)	11.1345(3)
α [°]	90	90	90
b [Å]	10.097(2)	10.9824(11)	7.7752(2)
β [°]	94.74(3)	98.471(3)	109.543(4)
c [Å]	20.215(4)	11.8799(11)	13.8287(4)
γ [°]	90	90	90
Volume [Å^3]	2807.4(10)	3361.4(5)	1128.22(5)
Z	4	8	4
ρ (calcd.) [Mg/m^3]	1.154	1.208	1.256
μ [mm^{-1}]	0.212	0.163	0.619
F(000)	1056	1280	456
Crystal size [mm]	0.5 × 0.09 × 0.08	0.5 × 0.2 × 0.2	0.24 × 0.16 × 0.03
θ range for data collection [°]	1.86 to 23.67	1.58 to 30.50	4.21 to 75.53
Index ranges	$-15 \le h \le 14$	$-37 \le h \le 37$	$-13 \le h \le 13$
	$-11 \le k \le 11$	$-15 \le k \le 15$	$-5 \le k \le 9$
	$-21 \le l \le 22$	$-16 \le l \le 16$	$-17 \le l \le 16$
Reflections collected	16899	27747	10717
Independent reflections	4218 [R(int) = 0.112]	5117 [R(int) = 0.033]	2239 [R(int) = 0.022]
Completeness	99.3% to θ = 23.67°	99.7% to θ = 30.00°	98.9% to θ = 67.5°
Absorption correction	numerical	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	0.9802 and 0.7756	0.9682 and 0.9088	1.00000 and 0.77727
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	4218/40/316	5117/0/175	2239/0/154
Goodness-of-fit on F^2	1.11	1.13	1.08
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0849	$R1$ = 0.0405	$R1$ = 0.0386
	$wR2$ = 0.240	$wR2$ = 0.109	$wR2$ = 0.108
R indices (all data)	$R1$ = 0.105,	$R1$ = 0.0558	$R1$ = 0.0416
	$wR2$ = 0.250	$wR2$ = 0.116	$wR2$ = 0.111
Largest diff. peak and hole [e Å^{-3}]	0.59 and –0.49	0.48 and –0.19	0.21 and –0.20

B), 20.2 (6%), 23.9 (7%), 24.1 (7%), 37.8 (2%), 51.8 (2%). Within a few days a small part of the substance crystallized and was separated from the solution and identified as **5b** by crystal structure analysis. The crystal data are compiled in Table 2, and selected bond lengths and angles are given in Figure 1. The NMR spectroscopic data of **5b** were obtained after TLC separation on silica gel with 10% ethyl acetate/hexane (1:9). ^{1}H NMR ($CDCl_3$): δ = 0.02 (s, 18 H, 2 $SiMe_3$), 1.30 (s, 9 H, CMe_3), 1.32 (t, ^3J = 7.1 Hz, 6 H, CH_3), 2.26 (s, 1 H, 3-H), 3.95–4.25 (m, 4 H, OCH_2), 7.13 (d, ^3J = 8.3 Hz, 1 H, 4-H), 7.62 (dd, ^3J = 8.3 Hz, $^4J_{P,H}$ = 6.0 Hz, 1 H, 5-H), 8.14 (v. br. s, NH), 10.76 (br. s, OH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 24.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{41}NO_5PSi_2$ [M – H]$^-$ 486.2266; found 486.2253; calcd. for [M – H – C_2H_4]$^-$ 458.1942; found 458.1948. The side products **A** and **B** were identified as aryl–*t*BuP(O)(OEt) species.[24] ^{13}C NMR ($CDCl_3$): **A**: δ = 23.23 (s, C*Me*$_3$), 35.13 (d, $^1J_{P,C}$ = 98.2 Hz, *C*Me$_3$) ppm, C_q-1 superimposed; **B**: δ = 23.35 (s, C*Me*$_3$), 35.22 (d, $^1J_{P,C}$ = 99.5 Hz, *C*Me$_3$), 99.09 (d, $^1J_{PC}$ = 103.5 Hz, C_q-1) ppm. HRMS (ESI): calcd. for $C_{18}H_{29}NO_4P$ [M – H]$^-$ 354.1840; found 354.1837. A minor signal set ($\Delta\delta^1$H ≈ 0.01–0.02 ppm, δ^{31}P = 24.1 ppm) belongs to the 3-trimethylsilylmethyl derivative. HRMS (ESI): calcd. for $C_{19}H_{33}NO_5PSi$ for [M – H$^+$]$^-$ 414.1871; found 414.1838; calcd. for [M – H – C_2H_4]$^-$ 386.1547; found 386.1543.

2-*tert*-Butyl-4-hydroxy-5-methyl-1*H*-1,3-benzazaphosphole (6): (a) A solution of pure *trans*-**3b** (1.3 g, 3.74 mmol) in diethyl ether was added in small portions at 0 °C to $LiAlH_4$ tablets (430 mg, 11.4 mmol) in diethyl ether (20 mL). This reaction mixture was stirred at room temperature for 3 d. Then, degassed water was added dropwise until the evolution of H_2 gas had ceased. The solids were removed by filtration and washed thoroughly with diethyl ether. The organic layer was dried with Na_2SO_4, filtered, and concentrated to give a colorless solid (654 mg), which was crystallized from THF/hexane to give colorless **6** (500 mg, 60%); mp. 134–135 °C. The data of single crystals grown by slow concentration of a C_6D_6 solution in a plastic-capped NMR tube are compiled in Table 2, and selected bond lengths and angles are given in Figure 2. ^{1}H NMR (C_6D_6): δ = 1.20 (d, $^4J_{P,H}$ = 1.2 Hz, 9 H, CMe_3), 2.19 (s, 3 H, 5-CH_3), 4.96 (br. s, half-width = 12 Hz, OH), 6.84 (dd, ^3J = 8.2 Hz, $^4J_{P,H}$ = 1.3 Hz, 1 H, 7-H), 7.05 (d, ^3J = 8.2 Hz, 1 H, 6-H), 8.40 (v. br. s, half-width = 18 Hz, NH) ppm. ^{13}C{^{1}H} NMR (DEPT, C_6D_6): δ = 15.91 (d, ^4J = 0.6 Hz, 5-CH_3), 31.87 (d, ^3J = 9.2 Hz, C*Me*$_3$), 36.24 (d, ^2J = 14.0 Hz, C_qMe$_3$), 106.62 (s, C-7), 113.06 (d, ^3J = 6.5 Hz, C_q-5), 129.14 (d, ^4J = 2.5 Hz, C-6), 130.42 (d, ^1J = 40.9 Hz, C_q-3a), 144.11 (d, ^2J = 4.7 Hz, C_q-7a), 154.24 (d, ^2J = 12.6 Hz, C_q-4), 188.94 (d, ^1J = 57.3 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR: δ = 51.5 (C_6D_6), 48.0 ($CDCl_3$) ppm. MS (EI, 70 eV, 100 °C): *m*/*z* (%) = 222 (13) [M]$^+$, 221 (75) [M]$^+$, 206 (100), 168 (30), 136 (33). HRMS (ESI, MeOH/H_2O, HCOOH): calcd. for $C_{12}H_{17}NOP$ [M + H]$^+$ 222.10423; found 222.10432. (b) A solution of *t*BuLi in pentane (3.6 mL, 1.9 M, 6.9 mmol) was added at –80 °C to an ethereal solution (25 mL) of **2b** (0.79 g, 2.3 mmol) and $ClSiMe_3$ (0.9 mL, 6.9 mmol). The mixture was slowly warmed to room temperature and stirred overnight. The crude product was added slowly to $LiAlH_4$ (0.26 g, 6.9 mmol) in diethyl ether (150 mL) at 0 °C. The

mixture was stirred at room temp. for 2 d, air-free water was added until the hydrogen evolution had ceased, and the mixture was filtered. ^{31}P NMR spectroscopy showed the signal of **6** (28%) along with the signals of primary (δ = –173.4 ppm, 11%) and secondary phosphanes (δ = –84.3 ppm, 8%; –67.1, 6%) and further side products. The diethyl ether was removed under vacuum, and the residual pale yellow oil was separated by silica gel column chromatography with 15% ethyl acetate/hexane for elution. Compound **6** was collected along with 2-methyl-5-(neopentylamino)phenol; the crude product was treated with 10% aqueous sulfuric acid, washed with a small amount of water, and dried with Na_2SO_4 (yield 98 mg, 19% referred to **2b**). The NMR spectroscopic data are in good agreement with those given above.

2-Methyl-5-(neopentylamino)phenol: ^{1}H NMR (C_6D_6): δ = 0.81 (s, 9 H, CMe_3), 2.09 (s, 3 H, Me), 2.67 (s, 2 H, NCH_2), 5.89 (d, ^4J = 2.3 Hz, 1 H, 2-H), 6.12 (dd, ^3J = 8 Hz, ^4J = 2.3 Hz, 1 H, 6-H), 7.06 (d, ^3J = 8.3 Hz, 1 H, 5-H) ppm. The formation of this compound is attributed to the reduction of unconverted **2b**.

Diethyl {2-Hydroxy-3-methyl-6-[2′-(trimethylsilyl)benzamido]-phenyl}phosphonate (7): A solution of *t*BuLi in pentane (1.6 M, 2.85 mL, 4.56 mmol) was added dropwise to *i*Pr$_2$NH (0.39 mL, 2.77 mmol) in diethyl ether (5 mL) at –30 °C. After 30 min, this mixture was added slowly to a solution of **2c** (500 mg, 1.38 mmol) in Et_2O (10 mL) at –78 °C. After a few minutes, a yellow precipitate formed. Stirring was continued as the mixture warmed to room temperature (overnight). Then, after the mixture was cooled to –30 °C, excess Me_3SiCl (0.58 mL, 4.57 mmol) was added, and the mixture was warmed to room temperature and stirred for 4 h. The precipitate was removed by filtration and washed with diethyl ether; the pale yellow filtrate was concentrated under vacuum and purified by column chromatography. Elution with 2% ethyl acetate/hexane gave **7** (170 mg, 28%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ = 0.37 (s, 9 H, $SiMe_3$), 1.27 (t, ^3J = 7.1 Hz, 6 H, CH_3), 2.23 (s, 3 H, 2-CH_3), 4.09 (ddq, ^2J = 10.2 Hz, $^3J_{P,H}$ = 8.5 Hz, ^3J = 7.1 Hz, 2 H, H_a of OCH_2), 4.20 (ddq, ^2J = 10.2 Hz, $^3J_{P,H}$ = 7.9 Hz, ^3J = 7.1 Hz, 2 H, H_b of OCH_2), 7.35 (d, ^3J = 8.2 Hz, 1 H, 4-H), 7.44, 7.48 (2 superimposed td, ^3J = 7.5 Hz, $^3J \approx 7$ Hz, ^4J = 1.6 Hz, 1 H, 4′-H, 5′-H), 7.62–7.74 (m, 3 H, 5-H, 3′-H, 6′-H), 8.45 (s, 1 H, NH), 10.78 (s, 1 H, OH) ppm. ^{13}C{^{1}H} and DEPT-135 NMR ($CDCl_3$): δ = –0.33 (d, J = 5 Hz, $SiMe_3$), 15.72 (d, ^3J = 5.2 Hz, CH_3), 15.84 (s, CH_3), 63.05 (d, ^2J = 4.3 Hz, OCH_2), 98.51 (d, ^1J = 173.5 Hz, C_q-1), 113.43 (d, ^3J = 10.4 Hz, C-5), 122.74 (d, ^3J = 11.8 Hz, C_q-3), 125.19, 128.53, 129.76, 135.54 (C-6′, C-5′, C-4′, C-3′), 136.12 (C-4), 137.23 (s, C_q-6), 140.80, 141.71 (C_q-1′, C_q-2′), 160.50 (d, ^2J = 5.3 Hz, C_q-2), 168.09 (CO) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 23.2 ppm. HRMS (ESI, MeOH, NaOAc): calcd. for $C_{21}H_{30}NNaO_5PSi$ [M + Na]$^+$ 458.1523; found 458.1526.

5-(Benzylamino)-2-methylphenol (8) and 5-Methyl-4-hydroxy-2-[2-(trimethylsilyl)phenyl]-1*H*-1,3-benzazaphosphole (9): A solution of crude **7**, containing **1c**, was prepared as described above by lithiation of **2c** (4.81 g, 13 mmol) in Et_2O (30 mL) at –78 °C with a solution formed from *t*BuLi (1.6 M in pentane, 27.3 mL, 43 mmol) and *i*Pr$_2$NH (3.90 mL, 27 mmol) in diethyl ether and subsequent reaction with $ClSiMe_3$ (4.9 mL, 44 mmol). To avoid the loss of **7** during workup, the crude product was directly subjected to reduction. The ethereal solution was added in small portions to $LiAlH_4$ (1.5 g, 39 mmol) in THF (20 mL) at 0 °C. This reaction mixture was stirred at room temperature for 3 d. Then, the mixture was cooled to 0 °C, and degassed water was added dropwise until the evolution of H_2 gas had ceased. The solid was removed by filtration, and the filtrate was concentrated to give a yellow oil. ^{1}H NMR spectroscopy revealed strong signals for **8** and weak signals for **9**. The extraction of the crude product with diethyl ether led to the enrichment of **8**, which crystallized from a concentrated toluene solution; m.p. 138–139 °C (yield not determined). The crystal data are compiled in Table 2, and selected bond lengths and angles are given in Figure 4. The removal of the solvent from the yellow mother liquor led to a sticky residue, which according to the NMR spectra consisted mainly of **8** with a small amount of **9** (δ^{31}P = 59.1 ppm) and traces of two P^{V}OEt compounds (δ^{31}P = 8.1 and 3.1 ppm). An attempt to separate **9** by silica gel column chromatography with up to 30% ethyl acetate/hexane failed. Compound **8**: ^{1}H NMR ($CDCl_3$): δ = 2.12 (s, 3 H, 2-CH_3), 3.3 (v. br., NH, OH), 4.28 (s, 2 H, NCH_2), 6.14 (d, ^4J = 2.2 Hz, 1 H, 6-H), 6.18 (dd, ^3J = 8.1 Hz, ^4J = 2.2 Hz, 1 H, 4-H), 6.89 (d, ^3J = 8.1 Hz, Hz, 1 H, 3-H), 7.26–7.38 (m, 5 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 14.78 (2-CH_3), 48.66 (NCH_2), 100.15 (C-6), 105.95 (C-4), 112.68 (C_q-2), 127.21 (C-*p*), 127.51, 128.60 (2 C-*o*, 2 C-*m*), 131.36 (C-3), 139.24 (C_q-*i*), 147.50 (C_q-5), 154.59 (C_q-1) ppm. HRMS (ESI, MeOH, NaOAc): calcd. for [M + H]$^+$ 214.12264; found 214.12271; calcd. for [M + Na]$^+$ 236.10459; found 236.10471. $C_{14}H_{15}NO$ (213.28): calcd. C 78.84, H 7.09, N 6.57; found C 79.10, H 7.43, N 6.33. Compound **9**: ^{1}H NMR ($CDCl_3$): δ = –0.07 (s, $SiMe_3$), 2.27 (s, 2-Me), 6.69 (d, $^3J \approx 8$ Hz, 7-H), 6.95 (d, $^3J \approx 8$ Hz, 6-H), 7.70–7.73 (2 d, 3′-H, 6′-H), 9.55 (br. s, OH) ppm; the other signals are superimposed. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –1.56 (d, ^5J = 2.6 Hz, $SiMe_3$), 15.11 (2-Me), 106.18 (C-7), 112.43 (d, ^3J = 7.7 Hz, C_q-5), 129.11 (C-6), 130.59 (d, ^1J = 40.0 Hz, C_q-3a), 143.40 (d, ^2J = 5.5 Hz, C_q-7a), 152.73 (d, ^2J = 12.0 Hz, C_q-4), 173.36 (d, ^1J = 50.2 Hz, C_q-2); 2-aryl signals uncertain in the presence of aryl signals of impurity **7**: 125.37, 128.83 (d, J = 2.6 Hz), 129.2 (superimposed), 131.80 (br.), 134.88 (d, J = 16.4 Hz, C_q-1′), 136.32 ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 59.1 ppm.

Crystal Structure Analysis of 5b, 6, and 8: The crystal data are summarized in Table 2. The diffraction data for **5b** were recorded at –103 °C with a STOE-IPDS 2T diffractometer with graphite-monochromated Mo-K_α radiation. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques (SHELXL-97).[28] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms at N1 and O1 were found and refined isotropically without any restraints. Methyl groups were refined as idealized rigid groups allowed to rotate but not tip. Other hydrogen atoms were placed at calculated positions and refined by using a riding model. One ethyl substituent (C14, C15) is disordered over two positions with 60 and 40% occupancy, respectively. The diffraction data for **8** were recorded at –173 °C with an Oxford Diffraction Nova A diffractometer with mirror-focused Cu-K_α radiation, and those for **6** were recorded at –130 °C with a Bruker SMART 1000 CCD diffractometer with monochromated Mo-K_α radiation. The structure solutions and refinements proceeded as above, except that the solvent of **6** required special attention; one of the two half-molecules of deuteriobenzene had to be removed with the SQUEEZE[29] routine because of severe disorder.

CCDC-1007401 (for **5b**), -1000343 (for **6**), and -1000342 (for **8**) contain 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.

Supporting Information (see footnote on the first page of this article): Supplementary experimental data for **3a**, **4a**, **2b**$_{OSi}$, and **3b**$_{OSi}$; ^{13}C NMR spectra of **1a** and **1b**; ^{1}H and ^{13}C NMR spectra of **1c**, **2a**–**2c**, **3a**, **3b**, **4a**, **6**, **7**, and **8**; ^{31}P NMR spectra of P compounds; crystal packing of **8**.

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