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Bulky *N*-Substituted 1,3-Benzazaphospholes: Access via Pd-Catalyzed C−N and C−P Cross Coupling, Lithiation, and Conversion to Novel P═C−P*t*Bu$_2$ Hybrid Ligands

Bhaskar Reddy Aluri,[†] Markus K. Kindermann,[†] Peter G. Jones,[‡] Ina Dix,[§] and Joachim Heinicke*,[†]

Institut für Biochemie - Anorganische Chemie Ernst-Moritz-Arndt-Universität Greifswald, Felix-Hausdorff-Str. 4, D-17487 Greifswald, Germany, Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany, and Institut für Anorganische Chemie, Universität Göttingen, Tammannstr. 4, 37077 Göttingen, Germany

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The syntheses of novel bulky *N*-substituted 1,3-benzazaphospholes are presented, together with their reactions with *tert*-butyllithium and coupling with *t*Bu$_2$PCl to novel *P*,*P*′-hybrid ligands that combine the highly basic and bulky di-*tert*-butylphosphanyl group with π-acidic low-coordinated phosphorus. The syntheses start with the preparation of new *N*-secondary 2-bromoanilines **1** by reduction of *N*-acyl 2-bromoanilides or more generally by Pd-catalyzed selective monoamination of *o*-dibromobenzene, followed by Pd-catalyzed C−P coupling with P(OEt)$_3$ to the respective 2-anilino-phosphonates **2**. The next steps are reduction to 2-phosphanylanilines **3** and condensation with Me$_2$NCH(OMe)$_2$, which leads via phosphaalkenes **4** to the corresponding *N*-substituted benzazaphospholes **5**. The reaction with *t*BuLi depends on the steric demand of the N substituent. Methyl, neopentyl-, and mesityl-derivatives were converted to P═C Li species **6** and coupled with *t*Bu$_2$PCl to novel P═C−P*t*Bu$_2$ ligands **7**, whereas *N*-adamantyl and *N*-2,6-diisopropylphenyl-derivatives prefer addition of *t*BuLi at the P═C bond to form dihydroderivatives. The chemical shifts of the low-coordinated phosphorus of **5** and **7** were found to reflect electronic and steric effects of the N substituents. The comparison of the crystal structures of *N*-neopentyl-1,3-benzazaphospholes **5** and **7** gives evidence of steric repulsion between the adjacent di-*tert*-butyl and neopentyl groups by the preferred anti orientation of the *P*-*tert*-butyl groups and moderate deviations of C2 and P3 of **7b** from the ring plane.

Introduction

Trivalent phosphorus compounds are extremely versatile ligands for coordination chemistry and find use in homogeneous transition-metal catalysis by stabilizing metals in low-valence states; they present versatile tuning abilities via steric and electronic properties.[1] Bulky and basic phosphanes are currently attracting particular attention,[2] but the endeavor to explore the potential of P═C compounds, electron-rich aromatically stabilized phospholides, and sandwich complexes thereof, or electron-deficient neutral P═C systems, is also evident and has been highlighted in recent overviews.[3–5] Catalysis with electron-deficient σ^2-*P*-ligands had

* To whom correspondence should be addressed. E-mail: heinicke@uni-greifswald.de.
† Ernst-Moritz-Arndt-Universität Greifswald.
‡ Technische Universität Braunschweig.
§ Universität Göttingen.

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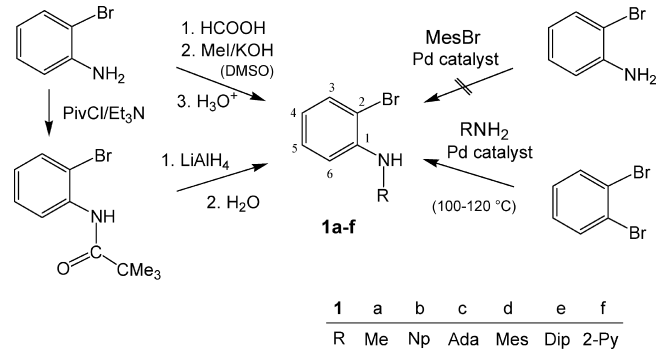
been rather rare,[6,7] but current studies with diphenylphosphanyl-phosphaalkene σ^3/σ^2-*P*,*P*′-hybrid ligands are promising and have led to isolable Pd(II) and Au(I) *P*,*P*′-chelate complexes that are catalytically active in various reactions.[8] In studies on anellated heterophospholes, particularly 1,3-benzazaphospholes (L), we obtained stable $LM(CO)_5$ complexes (M = Cr, Mo, W) and detected π-acidic properties of the double-bonded phosphorus.[9,10] Coordination of transition metals in higher oxidation numbers to neutral benzazaphospholes has not yet been observed, only to benzazaphospholide anions.[10,11] Even $[Rh(COD)Cl]_2$ did not react with 1*H*-1,3-benzazaphospholes except by heating in the presence of base. The rather-low stability of complexes of benzazaphospholes with transition-metal cations, combined with their good π-acceptor properties toward zerovalent metals, should allow catalyst stabilization by 2-phosphanyl-benzazaphosphole ligands. Reductive elimination may here lead to hemilabile *P*,*P*′-chelates, which, after oxidative addition, liberate a coordination site for substrate binding. This prompted us to extend the studies on benzazaphospholes to 2-phosphanyl derivatives as potential *P*,*P*′-hybrid ligands. 2-Di-*tert*-butylphosphanyl derivatives with bulky *N*-substituents, including *N*-aryl groups, were envisaged because bulky 2-phosphanyl-substituted *N*-aryl-pyrrols, -indoles, -imidazoles, or -benzimidazoles form particularly efficient palladium C−C and C−N cross-coupling catalysts.[12]

In this article, we report on a new route to *N*-substituted benzazaphospholes, the lithiation of the heterocycles with *t*BuLi, and coupling of 2-lithiobenzazaphospholes with tBu_2PCl to form novel *P*,*P*′-hybrid ligands. Alternative additions of *t*BuLi at the P=C bond and methods of achieving controlled CH metalation or addition will be reported separately.[13]

Results and Discussion

We recently reported a convenient access to 1*H*-1,3-benzazaphospholes by reductive cyclization of 2-phosphonoanilides, but *N*-substituted derivatives have so far been obtained only by multistep procedures starting with dilithiation of *N*-methyl-2-bromoaniline.[14] *N*-Alkylation, a convenient tool for modifying 1*H*-indoles,[15] failed for 1*H*-1,3-benzazaphospholes because of the strong preference for P alkylation, even after blocking the P lone-electron pair by coordination, for example, to $W(CO)_5$.[10] Therefore, a new more generally applicable strategy for the synthesis of *N*-substituted benzazaphospholes was developed, which is suitable also for bulky *N*-alkyl or *N*-aryl derivatives. The new synthesis of *N*-substituted benzazaphospholes comprises four steps: preparation and phosphonylation of *N*-secondary 2-bromoanilines, reduction of 2-phosphonoanilines, and cyclocondensation of the resulting 2-phosphanylanilines with orthoformate.

Scheme 1. Synthesis of *N*-Secondary 2-Bromoanilines



***N*-Secondary 2-Bromoanilines.** The *N*-secondary 2-bromoanilines **1a**−**e** (R = methyl, neopentyl, 1-adamantyl, mesityl, 2,6-diisopropylphenyl) used in this study have (except for **1a**) not yet been reported. Attempts at *N*-alkylation of 2-bromoformanilide by neopentyl bromide or neopentyl tosylate in DMSO/KOH (up to 140 °C) failed, but **1b** was easily accessed by pivaloylation of 2-bromoaniline and reduction with $LiAlH_4$ under mild conditions. **1c**−**e** were synthesized by Pd-catalyzed C−N cross coupling, which proved to be a suitable route to bulky derivatives. Whereas amination of mesitylbromide with 2-bromoaniline could not be achieved, *o*-dibromobenzene was found to undergo selective monoamination with bulky primary amines or anilines (Scheme 1). Screening of the coupling with mesitylamine for various phosphane−Pd catalysts gave good results with tri*tert*-butylphosphane, tri*o*-tolylphosphane, and BINAP (Table 1). The latter gave the best yields of **1d** and was therefore also used in the synthesis of **1c**. For **1e**, better results were obtained with the DPPF ligand. The pyridylaniline **1f**, prepared until now from 1,2-bromoiodobenzene,[16] was also synthesized with high selectivity and yield from *o*-dibromobenzene and 2-aminopyridine with palladium catalysts formed from $Pd_2(dba)_3$ and BINAP or DPPF.

Phosphonylation of *N*-Secondary 2-Bromoanilines. The phosphonylation of *N*-secondary 2-bromoanilines was first studied with **1a**, using di- and triethyl phosphite and varying

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Table 1. Synthesis of **1c**−**f** by Pd-Catalyzed Aryl Aminations[a]

o-$C_6H_4Br_2$, NaO*t*Bu (mmol)	RNH_2, (mmol)	Pd cmpd. (mol%), ligand (mol%)	conditions (°C, h)	product yield (%)[c]
4.23, 4.23	$MesNH_2$ 4.23	$Pd(OAc)_2$ (3.0), P(*o*-Tol)$_3$ (6.0)	120, 48	**1d** < 10
21.2, 25.4	$MesNH_2$ 21.2	$Pd_2(dba)_3$ (1.5), P(*o*-Tol)$_3$ (3.0)	125, 14	**1d** 23
8.47, 9.32	$MesNH_2$ 8.47	$Pd_2(dba)_3$ (1.0), *t*Bu_3P (2.5)	125, 14	**1d** 22
0.88,[b] 1.03	$MesNH_2$ 0.74	$Pd_2(dba)_3$ (5.0), BINAP (7.5)	100, 14	**1d** 70
1.58, 1.85	$AdaNH_2$ 1.32	$Pd_2(dba)_3$ (5.0), BINAP (7.5)	100, 14	**1c** 77
0.67, 0.78	$DipNH_2$ 0.56	$Pd_2(dba)_3$ (5.0), BINAP (7.5)	100, 14	**1e** 79
0.67, 0.78	$DipNH_2$ 0.56	$Pd_2(dba)_3$ (5.0), DPPF (7.5)	100, 14	**1e** 80
1.27, 1.48	2-$PyNH_2$ 1.06	$Pd_2(dba)_3$ (5.0), BINAP (7.5)	100, 14	**1f** 94
1.27, 1.48	2-$PyNH_2$ 1.06	$Pd_2(dba)_3$ (5.0), DPPF (10)	100, 14	**1f** 94

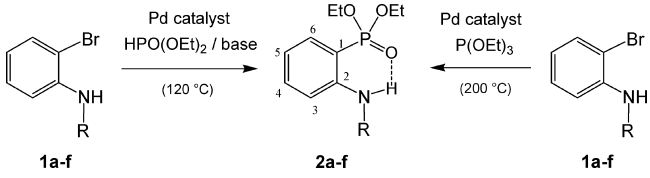
[a] Solvent toluene; abbreviations: Mes mesityl, Ada 1-adamantyl, Dip 2,6-diisopropylphenyl, Py pyridyl; BINAP, 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl; DPPF, diphenylphosphanylferrocene. [b] Excess (20%) versus mesitylamine. [c] Yield after isolation by column chromatography.

Table 2. Pd-Catalyzed C−P Coupling of **1a** with Di- or Triethyl Phosphite to **2a**[a]

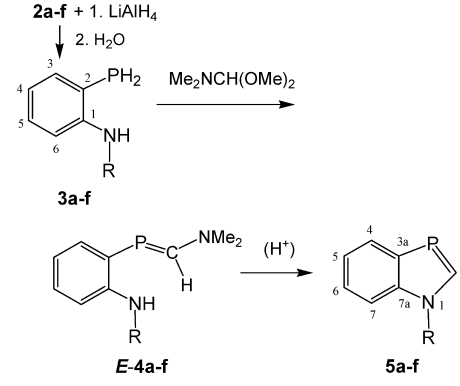
P compd. mmol (eq)	Pd compd. (mol%), Ligand (mol%)	base (eq)	conditions (°C, h)	yield (%)
$HPO(OEt)_2$ 1.18 (1.1)	$Pd(PPh_3)_4$ (4)	Et_3N (1.61)	120, 24	32
$HPO(OEt)_2$ 2.41 (1.5)	$Pd_2(dba)_3$ (1.5), P(*o*-Tol)$_3$ (6)	NaO*t*Bu (2.4)	120, 12	20
$HPO(OEt)_2$ 6.45, (1.2)	$Pd_2(dba)_3$ (2), P(*o*-Tol)$_3$ (6)	NaO*t*Bu (6.45)	120, 12	50
$HPO(OEt)_2$ 1.18 (1.1)	$Pd_2(dba)_3$ (2), BINAP (3)	NaO*t*Bu (1.4)	120, 12	0
$HPO(OEt)_2$ 1.18 (1.1)	$Pd_2(dba)_3$ (2), DPPF (3)	NaO*t*Bu (1.4)	120, 12	65
$HPO(OEt)_2$ 1.18 (1.1)	$Pd_2(dba)_3$ (2), *S*-PHOS[b](3)	NaO*t*Bu (1.4)	120, 12	12
$HPO(OEt)_2$ 2.41 (1.5)	$Pd_2(dba)_3$ (2), P(*o*-Tol)$_3$ (6)	NaO*t*Bu (2.4)	140, 12	≤5
$P(OEt)_3$ 1.61 (1.5)	$Pd_2(dba)_3$ (1.5), P(*o*-Tol)$_3$ (6)	NaO*t*Bu (1.6)	120, 12	0
$P(OEt)_3$ 1.18 (1.1)	$Pd(OAc)_2$ (5), $P(OEt)_3$[c]		200, 0.5	50

[a] Solvent: toluene, except last entry (neat); yield after isolation by thin layer chromatography, hexane/ethyl acetate (95:5). [b] 2-Dicyclohexylphosphanyl-2′,6′-dimethoxybiphenyl. [c] Acts as ligand and reactant, see column 1.

Scheme 2. Pd-Catalyzed Phosphonylation of 2-Bromoanilines



Scheme 3. Synthesis of 1,3-Benzazaphospholes via Phosphaalkenes



catalysts and conditions. Anhydrous nickel halides failed to catalyze the C−P coupling, but palladium catalysts were found to be active and less sensitive to the functional group. Use of $Pd(PPh_3)_4$ furnished the C−P coupling product with diethyl phosphite in toluene in the presence of triethylamine as a base, but the yield was low. In polar solvents such as NMP, the system became inactive. Use of tri*o*-tolylphosphane/$Pd_2(dba)_3$/NaO*t*Bu allowed coupling in yields up to 50% with 2 mol% Pd/6 mol% ligand at 120 °C/12 h. With DPPF as the ligand, 65% conversion was achieved, whereas *S*-PHOS or BINAP ligands were unsuitable (Table 2). Higher temperatures (140 °C) caused a dramatic decrease of the yield. Whereas replacement of diethyl phosphite by triethyl phosphite failed to couple **1a** with the phosphorus component in the presence of the $Pd_2(dba)_3$/tri*o*-tolylphosphane/NaO*t*Bu catalyst, phosphonoaniline **2a** was obtained in 50% yield by heating **1a** and $P(OEt)_3$ in the presence of $Pd(OAc)_2$ under harsh conditions (200 °C). $P(OEt)_3$ itself acts as a ligand. It is known to form a Pd(0) complex[17] that may be the true catalyst and be generated in small amounts throughout the reaction. With more bulky *N*-substituted 2-bromoanilines **1b**−**f** (Scheme 2), the yields of coupling products increased, so that this simple system was then preferred in the C−P coupling step. With excess triethyl phosphite and reaction times of 0.5−1 h, acceptable to excellent yields (72−94%) of **2b**−**f** were achieved, substantially more than for **2a**.

Synthesis of *N*-Substituted 1H-1,3-Benzazaphospholes. The 2-phosphono-anilines **2a**−**f** were converted to benzazaphospholes by reduction with $LiAlH_4$ to primary phosphanylanilines **3a**−**f** (**3a**[14]) and subsequent condensation with neat *N*,*N*-dimethyl formamide dimethylacetal (DMFA). The reaction proceeds via phosphaalkene intermediates ***E*-4a**−**f** to the 2-unsubstituted *N*-alkyl and *N*-aryl-1,3-benzazaphospholes **5a**−**f** (Scheme 3). The reaction rate depends strongly on the nature of the *N*-substituent, particularly for the second step. NMR control showed complete conversion of **3a** with DMFA to **5a** at room temperature in 2−3 d and rapid ring closure by lack of signals for intermediate **4a**. Monitoring the reactions of bulky *N*-secondary 2-phosphanylanilines with DMFA, however, displayed initially growing signals of ***E*-4b**−**e** at δ^{31}P 43.8−39.9, which later decreased or disappeared in favor of benzazaphosphole signals (δ^{31}P 66.4−78.1). Thus, after 24 h at 20 °C ***E*-4b** and **5b** were observed in a 2−3:1 molar ratio along with MeOH, Me_2NH, and unconverted

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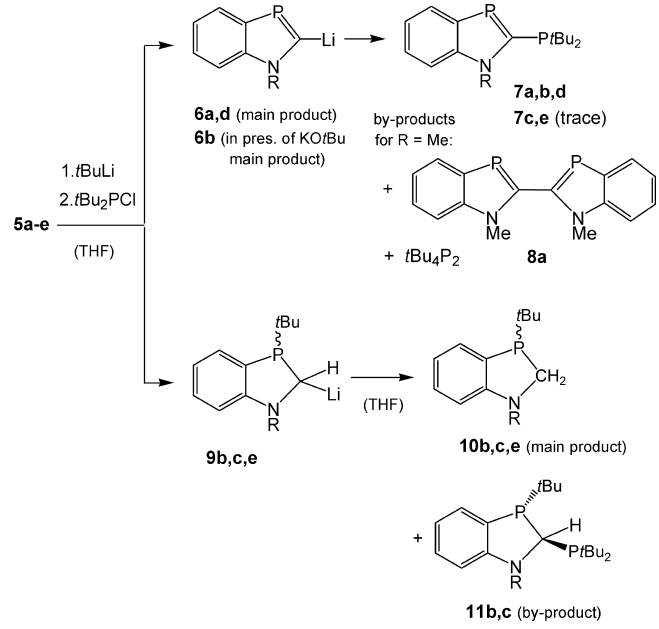
$Me_2NCH(OMe)_2$. The small value of the two-bond[31] P═C−^{1}H coupling (ca. 14 Hz) indicates the sterically preferred *E*-configuration.[18] Complete conversion to **5b**−**d** required heating at 40−60 °C for 5−7 d. In $CDCl_3$ solution, the reaction was faster and complete at room temperature in 3 d, which is attributed to catalysis by traces of acid. Acid-catalyzed ring closure was then applied to the sterically hindered Dip derivative *E*-**4e**, which did not convert to **5e** within 10 d at 60 °C and cyclized only on heating in the presence of ethereal HCl. The benzazaphospholes were easily purified by extraction of amine impurities with 10% aqueous sulfuric acid. The applicability of this treatment underlines the unusual stability of these heterocycles as compared to most P═C compounds, and the neutral properties give evidence of involvement of the nitrogen lone-electron pair into the aromatic π-system. The 2-pyridyl-substituted benzazaphosphole **5f**, obtained by heating of **3f** with DMFA for 7 d, is also stable toward acids but cannot be purified in this way because of the basic pyridyl group, and was thus distilled in high vacuum.

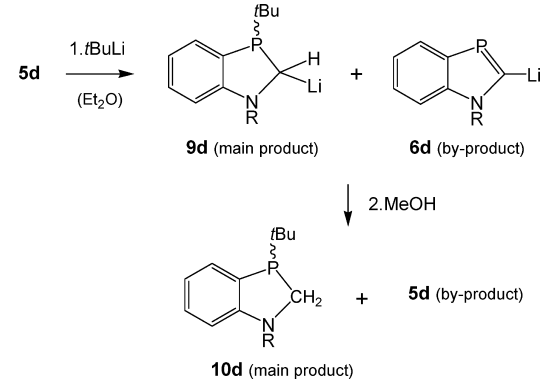
Lithiation of *N*-Substituted Benzazaphospholes and Reaction with tBu$_2$PCl. The introduction of various functional groups at position 2 of **5a** was achieved in good to reasonable yields by metalation with *t*BuLi at low temperature in THF or diethyl ether and coupling of the resulting P═CLi reagent **6a** with electrophiles.[9] The applicability of this strategy for the synthesis of bulky di-*tert*-butylphosphanyl-benzazaphospholes **7** with small to bulky alkyl and aryl groups at nitrogen was then studied.

Reaction of **6a** with tBu$_2$PCl in THF led preferably to 2-di-*tert*-butylphosphanyl-benzazaphosphole **7a** (Scheme 4), but minor amounts of (tBu$_2$P)$_2$ and **8a**, according to NMR data and a mass spectrum probably a bis(benzazaphosphole), were also formed and hint at metal−halogen exchange as a minor reaction. Lithiation in the presence of KO*t*Bu and coupling with excess tBu$_2$PCl suppressed this. The behavior of the bulkier *N*-substituted benzazaphospholes **5b**−**e** differs however to varying extents from that of **5a**. Steric bulk hinders CH-lithiation in the 2-position in favor of addition of *t*BuLi to the P═C bond, with a high preference for attack of the *tert*-butyl group at phosphorus. Thus, besides 2-lithiobenzaphospholes **6** the adducts **9** were formed, increasingly in the order R = mesityl < neopentyl ≪ 2,6-diisopropylphenyl < 1-adamantyl. Furthermore, the behavior depends on the solvent. ^{31}P NMR reaction control showed that the least hindered 1-mesityl-1*H*-1,3-benzazaphosphole (**5d**) reacts with *t*BuLi in THF almost exclusively to **6d**, but in diethyl ether to a mixture of **6d**, **9d**, **9d′**, and **10d** (relative signal intensities 17:25:8:50). Quenching the mixture with methanol converted **9d** and **9d′**, an unidentified minor lithiated species, quantitatively to **10d**. The ratio of **5d** to

Scheme 4. Reaction of Less (**5a**, **b**, **d**) or More (**5c**, **e**) Bulky *N*-Substituted Benzazaphospholes with *t*BuLi (in THF) and tBu$_2$PCl



Scheme 5. Reaction of **5d** with *t*BuLi (in Diethyl Ether) and Methanol



10d, that means C(2)-lithiation to addition, was then ca. 20:80% (by ^{1}H integration of CMe_3 singlets) (Scheme 5). Whereas lithiobenzazaphospholes **6** are stable to THF, the high content of **10d** even before the addition of methanol gives evidence that the major part of **9d**/**9d′** was converted to **10d** by deprotonation of ether, and thus that the reactivity of dihydrobenzazaphospholyl lithium species is high and comparable to that of branched alkyl lithium reagents.[19]

The behavior of 1-neopentyl-benzazaphosphole (**5b**) is more complicated than that of **5d**; **5b** displays competing CH-lithiation and addition of *t*BuLi at P═C even in THF, and subsequent reaction with tBu$_2$PCl led to a mixture of **7b**, **10b** and a minor diphosphane with phosphorus chemical shifts and J_{PP} coupling constants consistent with a 2-phosphanyl-dihydrobenzazaphosphole structure **11b**. A definite assignment, however, requires more-detailed investigations of *t*BuLi addition and subsequent phosphinylation reactions. A study of the possibility of controlled CH-lithiation of **5b** or addition of *t*BuLi[13] gave evidence that polar additives such

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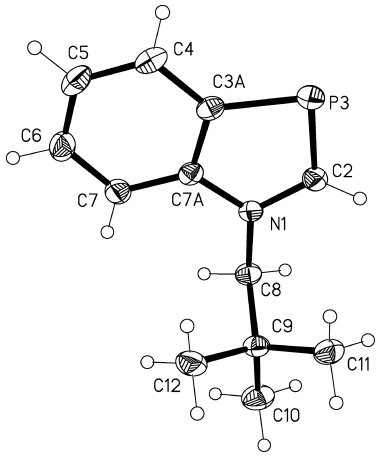

Figure 1. Molecular structure of **5b** (ellipsoids with 50% probability). Selected bond lengths (Angstroms) and angles (degrees): P3−C2 1.7102(14), P3−C3A 1.7815(15), C2−N1 1.3580(18), N1−C7A 1.3832(17), C3A-C7A 1.4155(19); N(1)−C(2)−P(3) 116.11(10), C(2)−P(3)−C(3A) 88.17(7), C2−N1−C7a 112.86(10), C2−N1−C8 121.92(12), C7A−N1−C8 125.69(11).

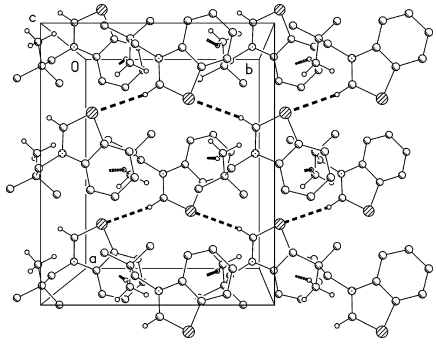

Figure 2. Packing of **5b** in the crystal. Layer at z ca. $^1/_4$; H contacts: C2−H2 0.95, H2···P3#1 2.94, C2···P3#1 3.8038(15) Å; C2−H2···P3#1 152.3. "Weak" interactions are indicated by thick dashed lines.

as *t*BuOK, which forms a Schlosser base,[19b] are favoring CH-metalation, whereas nonpolar solvents such as *n*-pentane shift the selectivity toward addition and make **5b** a case that allows reaction tuning for different product types. Thus, the synthesis of **7b** succeeded by metalation of **5b** with *t*BuOK/*t*BuLi and subsequent reaction with excess (for conversion with KO*t*Bu) $t\mathrm{Bu_2PCl}$. For the bulkier benzazaphospholes **5c** and **5e**, with *N*-adamantyl and *N*-2,6-diisopropyl substituents, the preference for addition was very strong even in THF, so that no attempts were made to force the reaction toward CH-metalation. Nevertheless, small amounts of **7c** and **7e** were detected by the characteristic phosphorus doublets with similar chemical shifts and $^2J_{PP}$ coupling constants, as observed for **7a**,**b** and **7d**.

Structural Aspects. The structure elucidation of the new compounds is based on conclusive multinuclear solution NMR data, for isolated compounds supplemented by HRMS data or satisfactory elemental analyses. For **5b** and **7b**, the crystal structures (Figures 1–3) were determined.

The NMR spectra exhibit features characteristic of the various compound types. In comparison to related *N*-alkyl- and *N*-aryl compounds, strong downfield shifts are observed for the protons in ortho position to the pyridylamino group of *N*-pyridyl species **1**−**5f** ($\Delta\delta > 0.8$). This effect exceeds by far the small downfield shifts of other benzene ring

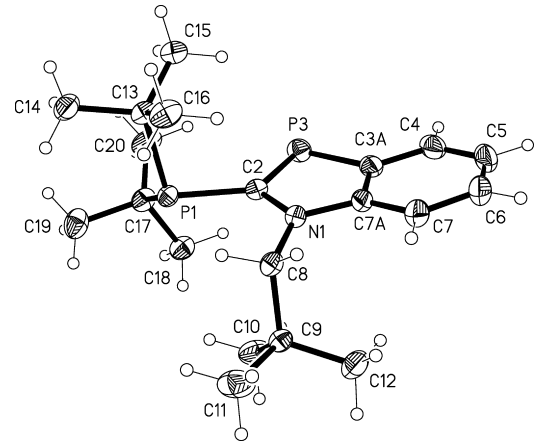

Figure 3. Molecular structure of **7b** (ellipsoids with 50% probability). Selected bond lengths (Angstroms) and angles (degrees): P3−C2 1.7295(13), P3−C3A 1.7717(14), C2−N1 1.3915(16), N1−C7A 1.3884(16), C3A−C7A 1.4064(19), P1−C2 1.8397(12), P1−C13 1.9059(13), P1−C17 1.9017(13); N1−C2−P3 113.21(9), C2−P3−C3A 89.81(6), C2−N1−C7A 112.86(10), C2−N1−C8 124.81(10), C7A−N1−C8 122.19(10), N1−C2−P1 118.58(9), P3−C2−P1 128.06(7).

protons caused by the electron-withdrawing *N*-pyridyl group, and is attributed to the proximity of the nitrogen lone-electron pair in cis coplanar rotamer populations. Also conspicuous are the downfield shifts of NH-signals of *N*-secondary phosphonoanilines **2** compared to those of 2-bromoanilines **1** ($\Delta\delta \approx 2.2$) or 2-phosphinoanilines **3** ($\Delta\delta \approx 2.4$), indicating increased NH-acidity by intramolecular hydrogen bonds. The structure elucidation of P═CH compounds is facilitated by the downfield doublet with an unusual $^2J_{PH}$ coupling constant, which also allows the *E*- and *Z*-configurations to be distinguished. In this way, the phosphaalkene intermediates **4** were detected. The $^2J_{PH}$ coupling constants of the P═CH proton signals of these compounds ($^2J_{PH2} \approx 14$ Hz) are typical of *E*-isomers[18] and much smaller than in the benzazaphospholes **5a**−**e** ($^2J_{PH2} = 49.8-54.4$ Hz) with *Z*-configuration. The phosphorus signals of **4**, confirmed by P−H coupled ^{31}P NMR, appear at δ 40−46 and decrease with the progress of the reaction in favor of benzazaphosphole signals. These absorb at lower field, which is consistent with cyclodelocalization of the increased π-electron density at phosphorus provided by the lone electron pair of nitrogen in β-position, resulting in a π-excess-type aromatic system, as shown by quantum chemical calculations.[20]The electronic impact of the N donor atom in N−C═P systems, responsible for the general strong upfield shift of **4** and **5** compared to phosphaalkenes and phosphabenzenes[18b] causes also a strong influence of the *N*-substituents on the phosphorus resonance. For **5a-e** the phosphorus chemical shift increases in the order **5c** < **5b** < **5a** < **5e** < **5d** < **5f** (δ^{31}P 66.4, 70.8, 72.6, 76.0, 78.1, 85.0) and is thus a direct probe for the electronic effect of the *N*-substituent. The branched alkyl group 1-adamantyl has the strongest +I effect, followed by neopentyl and methyl. The marginal decrease from *N*-methyl to *N*-mesityl and *N*-2,6-diisopropylphenyl substituents indicates a lack of

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Table 3. Crystal Data and Structure Refinement of **5b**, **7b**, and (tBu$_2$PHO·LiCl)$_4$

compound	**5b**	**7b**	(tBu$_2$PHO·LiCl)$_4$
empirical formula	$C_{12}H_{16}NP$	$C_{20}H_{33}NP_2$	$C_{32}H_{76}Cl_4Li_4O_4P_4$
fw	205.23	349.41	818.37
T (K)	133(2)	100(2)	100(2)
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*Pbca*	$P2_1/c$	*Fddd*
a (Å)	12.0011(14)	8.5309(3)	13.7123(4)
b (Å)	10.0307(12)	14.3944(3)	26.3955(8)
c (Å)	18.899(2)	17.0277(4)	26.7143(8)
α (deg)	90	90	90
β (deg)	90	102.702(2)	90
γ (deg)	90	90	90
V (Å^3)	2275.0(4)	2039.78(10)	9669.1(5)
Z	8	4	8
D_{calcd} (Mg m^{-3})	1.198	1.138	1.124
σ (mm^{-1})	0.203	1.912	3.694
F(000)	880	760	3520
θ range (deg)	2.16 to 30.50°	4.06 to 71.17°	3.99 to 69.74°
index ranges	$-15 \le h \le 17$, $-8 \le k \le 14$, $-26 \le l \le 26$	$-10 \le h \le 9$, $-17 \le k \le 17$, $-20 \le l \le 20$	$-16 \le h \le 15$, $-31 \le k \le 32$, $-32 \le l \le 32$
no. of reflns collected	17 887	28 965	39 203
no. of indep reflns (R_{int})	3463/0.0702	3847/0.0205	2262/0.0355
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF	1.031	1.076	1.079
R1, wR2 [$I > 2\sigma(I)$]	0.0402, 0.0997	0.0292, 0.0778	0.0244, 0.0666
R1, wR2 (all data)	0.0696, 0.1138	0.0316, 0.0794	0.0253, 0.0675
largest diff. peak/hole (e·Å^{-3})	0.392 and −0.184	0.298 and −0.212	0.325 and −0.218

mesomeric effects and a mutually rotated arrangement of benzazaphosphole and *N*-aryl π-planes. The considerably stronger downfield effect of the *N*-pyridyl group may be attributed partly to the electron-withdrawing character of the pyridine ring, partly to mesomeric effects. Coplanar populations are made possible by the lack of *o*-substituents and are manifested by the above-mentioned downfield shifts for protons adjacent to the pyridylamino group. C2-substituents have an even stronger influence on the phosphorus resonance than *N*-substituents. The 2-di-*tert*-butylphosphanyl groups of **7a**−**e** cause a strong downfield shift of the ring phosphorus signal, which increases markedly in the order **7a** (NMe, small) < **7d** (NMes, planar) < **7b** (NNp, primary alkyl) < **7e** (*N*-Dip, planar/bulky) ≪ **7c** (*N*-Ada, bulky *tert*-alkyl group) ($\Delta\delta^{31}$P 38.9, 43.1, 44.4, 49.5, 66.8) and thus may be regarded as indicator of the steric demand of the *N*-substituent. It is assumed that larger *N*-substituents push the bulky tBu$_2$P group toward the low-coordinate phosphorus atom so that the P lone electron pair of the basic phosphanyl group (rotamer population with electron lone pairs in the same direction) causes repulsion of π-density from the easily polarizable σ^2-P atom.

The carbon signals of benzazaphospholes, including that of P═C, are rather insensitive to electronic or steric effects of the *N*-substituents. The C2 resonance of **5a**−**f** appears in the region δ^{13}C 157.5−163.0 with the *N*-adamantyl compound at the upfield end. Replacement of hydrogen at C2 by the tBu$_2$P group causes similar changes of the chemical shifts ($\Delta\delta \approx 12$) as known for normal aromatic compounds (benzene versus tBu$_2$PPh[21] $\Delta\delta$ 10) but lithiation induces much stronger downfield shifts. The difference of δ^{13}C2(**6**) and δ^{13}C2(**5**) is 87−88, that between PhLi and benzene only 58. The general strong downfield shift is explained by repulsion of π-electron density by the negative charge at polar (sp^2)C−Li sites,[22] the increased effect in benzazaphospholes by the higher polarizability of π-systems containing elements of higher periods. The resulting decrease of total negative charge at C(2)Li may reduce the reactivity of **6** more than that of PhLi as compared to alkyllithium reagents and, in the case of additional steric hindrance, may contribute to low yields of coupling products.

Further structural information on bulkier *N*-substituted 1-neopentyl-benzazaphospholes with or without a 2-di-*tert*-butylphosphino group is given by the X-ray crystal structure analyses of **5b** and **7b**, respectively (Figures 1 and 3, crystal data in Table 3). The molecules of **5b** are arranged in chains parallel to the *y* axis by an H2···P contact of 2.94 Å that could be regarded as a weak hydrogen bond and a hint to slightly increased CH acidity and σ^2-P basicity,[5] which is not observed in phosphabenzenes.[3] The *tert*-butyl group of the neopentyl substituent is bent out of the plane (dihedral angle N1−C8−C9−C2 85.7(2)°) and allows for C11−H11B···π-interactions with the center of a six-membered ring (2.78 Å, angle 162°) of a neighboring molecule, leading to thick layers of molecules parallel to the *xy* plane at *z* ca. $^1/_4$ and $^3/_4$ (Figure 2). The bent arrangement of the neopentyl group in the solid state does not explain steric hindrance of the CH-lithiation in the 2-position. The steric effects observed in solution may be caused by rotation of the neopentyl group around the N−C bond. The bond lengths and angles lie in the usual ranges and are comparable with those in other benzazaphospholes.

In **7b**, there are no short H···P or H···N contacts, but the molecules are associated, as in **5b**, by short neopentyl H11A···π contacts (2.54 Å) to the center of the six-membered ring of a neighboring molecule, thereby forming chains parallel to the *y* axis. Bond lengths and angles are

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similar to those in **5b** except the N1−C2 bond, which is lengthened by 0.034 Å and the longest so far in all structurally characterized benzazaphospholes.[9–11,23] This is probably accounted for by steric hindrance between the 2-*t*Bu$_2$P and 1-neopentyl substituents, although the bulky tertiary butyl groups are turned away from each other. The angle C7A−N1−C8 is somewhat smaller than C2−N1−C8, whereas in **5b** the situation is the opposite. CMe$_3$ of neopentyl, despite being nearly perpendicular to the ring plane, is turned toward the six-membered ring side by about 10° (C7A−N1−C8−C9 −79.60(14)°). Much more pronounced is however the orientation of the *P*-*tert*-butyl groups toward the P3 side of the ring plane and the fact that the bulky groups are not arranged in an intersecting conformation with the ring plane. Instead, the P*t*Bu group at C17, on the same side as the *tert*-butyl end of the neopentyl group, is rotated further away (C17−P1−C2−N1 −149.16(9)°) than the other *P*-*t*Bu group at C13, which is arranged nearly perpendicular to the ring plane (C13−P1−C2−N1 95.38(10)°). The repulsion between the adjacent phosphanyl and neopentyl groups is further expressed (and diminished) by slight displacements of these substituents out of the plane of the five-membered ring (mean deviation 0.02 Å), C8 by 0.19 Å and P1 by 0.18 Å in the opposite direction. Also, P3 (by 0.19 Å) and C2 (by 0.20 Å) are slightly displaced out of the plane of the six-membered ring plus N1 (mean deviation 0.01 Å) of **7b**, whereas in **5b** such deviations are negligible; all nine ring atoms are coplanar to within 0.01 Å. As expected, the C−P−C angle between the two *t*Bu groups in **7b** (C13−P1−C17 110.74(6)°) is larger than the C−P−C angles between *t*Bu and C2 of the ring (C2−P1−C13 101.19(6), C2−P1−C17 105.55(6)°). In the opposite direction, the space occupied by the lone pairs, is not suitable for *P*,*P*′-chelate formation, but in solution rotation is still possible, as seen by the occurrence of each one averaged (C_6D_6) or broad (d_8-THF) signal for the *t*Bu(P) nuclei in the ^{1}H and the ^{13}C NMR spectra. The signal of the quarternary carbon of this group and the NCH$_2$ proton signals are strongly broadened.

Attempts to grow single crystals of *N*-aryl benzazaphospholes failed so far, and large crystals of **8d** obtained from THF displayed poor diffraction, possibly because of solvent disorder. A byproduct, (*t*Bu$_2$PHO–LiCl)$_4$, crystallized much better and was identified by X-ray diffraction as a μ_3-chloro tetramer with distorted cubane structure, shown here as rare example of structurally characterized phosphine oxide lithium chloride complexes (Figure 4). The molecule displays crystallographic *222* symmetry with a structure analogously to that of the known (HMPA–LiCl)$_4$ complex,[24a] whereas the electronically more similar (Me$_3$PO–LiCl)$_n$ displays a polymer chain with alternating chloro and alkoxy bridges[24b] and triethylphosphine oxide and LiCl form a [(LiCl)$_3$(Et$_3$PO)$_4$] cluster, which can be described as a distorted Li$_4$O$_4$ cluster with terminal chloride and one LiCl

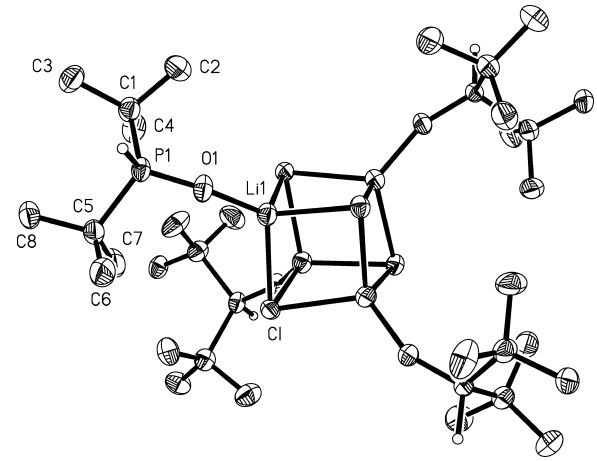

Figure 4. Distorted cubane structure of the byproduct (*t*Bu$_2$PHO-LiCl)$_4$ (ellipsoids with 50% probability). Selected bond lengths (Angstroms) and angles (degrees): Li−Cl 2.403(2), 2.394(2), 2.399(2), Li−O 1.835(2), P−O 1.4975(9); P−O−Li 154.80(9), Li−Cl−Li 79.13(8), 79.37(8), 79.82(8), Cl−Li−Cl 99.10(8), 99.75(8), 100.09(8).

omitted.[24c] The question as to why the more basic phosphine oxides form different cluster types with LiCl will require separate studies.

Conclusion

Benzazaphospholes with bulky *N*-substituents are accessible by a four-step synthesis comprising preparation of the corresponding *N*-secondary 2-bromoaniline by Pd-catalyzed monoamination of *o*-dibromobenzene (or an alternative method), followed by Pd-catalyzed phosphonylation with triethyl phosphite, reduction with LiAlH$_4$, and cyclocondensation using dimethylformamide dimethyl acetal. Introduction of functional groups by CH-lithiation and subsequent coupling with electrophiles is possible for nonbulky *N*-alkyl and *N*-aryl substituents (methyl, mesityl) and also allows the introduction of the bulky and *P*-basic *t*Bu$_2$*P*-substituent at position 2, with better yield for 2-lithio-*N*-mesityl-benzazaphosphole than for the *N*-methyl moiety. Bulky *N*-adamantyl and *N*-2,6-diisopropylphenyl substituents hinder CH-lithiation in position 2 in favor of *tert*-butylation at phosphorus, which, after subsequent treatment with *t*Bu$_2$PCl, led to only trace amounts of the corresponding 2-phosphanyl-benzazaphospholes. *N*-Neopentyl-benzazaphosphole occupies an intermediate position and reacts with *t*BuLi in THF to render a mixture of CH-lithiation and additions products. Preferential CH-lithiation was achieved by addition of KO*t*Bu, which then also allowed access to 2-di-*tert*-butylphosphanylated benzazaphosphole. Nonpolar solvents shift the reaction to addition.[13] The steric bulk of the *N*-substituent and the resulting preference for addition of *t*BuLi to the P═C bond are reflected in the difference $\Delta\delta^{31}$P of the phosphorus resonances of the double-bonded phosphorus of corresponding 2-di-*tert*-butylphosphino- and 2-unsubstituted benzazaphospholes. The availability of the novel 2-di-*tert*-butylphosphanyl-benzazaphosphole *P*,*P*′-hybrid ligands with *N*-alkyl and *N*-mesityl groups allows this combination of bulky and highly *P*-basic compounds with low-coordinated π-acidic phosphorus atoms to be investigated with respect to catalytic

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applications and stabilization of zerovalent catalyst metals by hemilabile complexes.

Experimental Section

General Remarks. All reactions were performed under an atmosphere of dry argon using Schlenk techniques. THF, ether, and hydrocarbons were dried over sodium ketyl and distilled before use. Reagents were used as purchased. NMR spectra were measured at 25 °C on a multinuclear FT-NMR spectrometer Bruker ARX300 at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. ^{1}H, ^{13}C, and ^{31}P chemical shifts are δ values and given in ppm relative to Me_4Si and H_3PO_4 (85%), respectively, as external standards. Assignment numbers of anilines, phosphonic acid esters, and benzazaphospholes follow the nomenclature (Schemes 1−3), for aryl and alkyl substituents *i*, *o*, *m*, *p*, and α, *β* etc. assignment indices are used. Coupling constants refer to H−H (^{1}H NMR) or P−C couplings (^{13}C NMR) unless stated otherwise. Relative intensities I_{rel} of ^{31}P signals of mixtures formed by competing CH-metalation and addition reactions of **5** and *t*BuLi refer to acquisition times 0.655 s and delays 2.0 s and do not represent quantitative molar ratios (^{31}P relaxation times T_1 for R_3P are 5−30 s).[25] Mass spectra were recorded on a single-focusing mass spectrometer AMD40 (Intectra). HRMS measurements were carried out in Göttingen with a double-focusing sector-field instrument MAT 95 (Finnigan) with EI (70 eV, PFK as reference substances) or with ESI in MeOH, MeOH/aqueous format or NH_4OAc or MeCN using a 7 T Fourier transfrom ion cyclotron resonance mass spectrometer APEX IV (Bruker Daltonics). Elemental analyses were carried out using an elemental analyzer LECO Model CHNS-932 under standard conditions. Melting points were determined in sealed capillaries under argon and are uncorrected.

***N*-Secondary 2-Bromoanilines.** 2-Bromo-trimethylacetanilide (yield 97%, mp 59 °C; MS (EI, 70 eV, 305 °C): *m*/*z* (%) = 257 (18) [M^+], 255 (17), 177 (10), 176 (100), 173 (48), 171 (48), 57 (73)) and 2-bromo-*N*-methylaniline (**1a**) were prepared as reported earlier.[26]

2-Bromo-*N*-2,2-dimethylpropyl-aniline (1b). A solution of 2-bromo-trimethylacetanilide (4.3 g, 16.7 mmol) in THF (15 mL) was added dropwise at 0 °C to $LiAlH_4$ tablets (0.7 g, 18.4 mmol). The mixture was stirred at room temperature for 1 day. Then, distilled water was added dropwise until the evolution of H_2 gas ceased. The solids were filtered off and washed with ether, and the filtrate was dried over Na_2SO_4 and concentrated in vacuum. The compound was purified by column chromatography on silica gel, 2% Et_2O/hexane, to give 1.76 g 1b as a colorless oil (62%). ^{1}H NMR ($CDCl_3$): δ 1.02 (s, 9H; CH_3), 2.93 (s, 2H; NCH_2), 4.3 (vbr, 1H; NH), 6.52 (td, ^3J = 7.7, ^4J = 1.5 Hz, 1H; H-4), 6.64 (dd, ^3J = 8.2, ^4J = 1.4 Hz, 1H; H-6), 7.15 (td, ^3J = 7.2, ^4J = 1.5 Hz, 1H; H-5), 7.40 (dd, ^3J = 7.9, ^4J = 1.5 Hz, 1H; H-3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.63 (CH_3), 31.91 (CMe_3), 55.66 (CH_2), 109.81 (C_q-2), 111.27 (CH-6), 117.26 (CH-4), 128.42 (CH-5), 132.29 (CH-3), 145.44 (C_q-1); MS (EI, 70 eV, 20 °C): *m*/*z* (%): 243 (16) [M^+], 241 (17) [M^+], 186 (98), 184 (100), 77 (16), 41 (17); Elemental analysis Calcd (%) for $C_{11}H_{16}BrN$ (242.16): C, 54.56; H, 6.66; N, 5.78. Found: C, 54.49; H, 6.89; N, 6.15.

***N*-Adamant-1-yl-2-bromoaniline (1c).** NaO*t*Bu (178 mg, 1.85 mmol), BINAP (61 mg, 7.5 mol%), and $Pd_2(dba)_3$ (60 mg, 5.0 mol%) was placed into an oven-dried Schlenk tube. 1-Adamantylamine (200 mg, 1.32 mmol), 1,2-dibromobenzene (0.19 mL, 1.58 mmol), and toluene (4 mL) were added. This mixture was heated at 100 °C for 14 h. After cooling to room temperature, the mixture was diluted with diethyl ether and filtered. The filtrate was concentrated and purified by chromatography on silical gel (0.063−0.100 mm) using 0.5% Et_2O/ hexane as eluant to give 310 mg (77%) of a colorless solid, mp = 113−114 °C; ^{1}H NMR ($CDCl_3$): δ 1.72 (br d, ^3J = 2.6 Hz, 6H; CH_2), 1.98 (br d, ^3J = 3.0 Hz, 6H; CH_2), 2.14 (br s, 3H; CH), 4.19 (br s; NH), 6.58 (td, ^3J = 7.9, 7.1, ^4J = 1.7 Hz, 1H; H-4), 7.06 (dd, ^3J = 8.2, ^4J = 1.7 Hz, 1H; H-6), 7.11 (td, ^3J = 8.2, 7.1, ^4J = 1.5 Hz, 1H; H-5), 7.43 (dd, ^3J = 7.9, ^4J = 1.5 Hz, 1H; H-3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 29.71 (CH), 36.43 (CH_2), 43.03 (CH_2), 52.65 (NC_q), 112.97 (C_q-2), 116.83 (CH-6), 118.39 (CH-4), 127.67 (CH-5), 132.66 (CH-3), 143.58 (C_q-1); MS Calcd for $C_{16}H_{20}BrN$: 305.1, 307.1, found (EI, 70 eV, 345 °C): *m*/*z* (%) = 307 (32) [M^+ for ^{81}Br], 305 (33) [M^+ for ^{79}Br], 250 (38) [M^+−57], 248 (37) [M^+−57], 169 (21), 135 (100).

***N*-Mesityl-2-bromoaniline (1d).** (a) BINAP (34 mg, 7.5 mol%), NaO*t*Bu (99 mg, 1.03 mmol), $Pd_2(dba)_3$ (33 mg, 5 mol%) were placed into an oven-dried Schlenk tube. Then 2,4,6-trimethylaniline (0.1 mL, 0.74 mmol), 1,2-dibromo benzene (0.1 mL, 0.88 mmol), and finally toluene (4.0 mL) were added. The reaction mixture was stirred at 100 °C overnight, and then the insoluble material was separated and washed thoroughly with ether. The solvent of the filtrate was removed in vacuum, and the residual crude compound was purified by chromatography on silica gel (0.063−0.100 mm mesh) using 0.5% ethyl acetate/hexane as eluant to give 170 mg (70%) colorless solid **1d**.

***N*-Mesityl-2-bromoaniline (1d).** (b) P(*o*-Tol)$_3$ (193 mg, 3 mol%), NaO*t*Bu (2.5 g, 25.4 mmol), $Pd_2(dba)_3$ (291 mg, 1.5 mol%), 2,4,6-trimethylaniline (3.0 mL, 21.2 mmol), 1,2-dibromobenzene (2.5 mL, 21.2 mmol), and toluene (40 mL) were allowed to react with stirring at 125 °C overnight. Work-up as described in (a) provided a brown oil containing unconverted dibromobenzene. This was removed in vacuum at 10^{-2} Torr/85 °C to give 1.4 g (23%) of colorless oily **1d**, which solidified on standing at room temperature, mp = 63 °C; ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 6H; *o*-CH_3), 2.30 (s, 3H; *p*-CH_3), 5.62 (br s; NH), 6.14 (dd, ^3J = 8.2, ^4J = 1.5 Hz, 1H; H-6), 6.56 (td, ^3J = 8.0, 7.6, ^4J = 1.5 Hz, 1H; H-4), 6.94 (s, 2H; 2-*m*), 7.00 (td, ^3J = 8.2, 7.3, ^4J = 1.5 Hz, 1H; H-5), 7.46 (dd, ^3J = 8.0, ^4J = 1.5 Hz, 1H; H-3); ^{13}C{^{1}H} (DEPT135) NMR ($CDCl_3$): δ 18.06 (*o*-CH_3), 20.95 (*p*- CH_3), 109.32 (C_q-2), 112.42 (CH-6), 118.34 (CH-4), 128.29 (CH-5), 129.24 (CH-*m*), 132.40 (CH-3), 134.85 (C_q-*p*), 136.14 (C_q-*i*), 136.42 (C_q-*o*), 143.62 (C_q-1); MS (EI 70 eV, 20 °C): *m*/*z* (%) = 292 (13) [M+H$^+$], 291 (98) [M^+], 290 (18) [M^+], 289 (100) [M^+], 210 (43), 208 (39), 195 (69), 194 (57), 193 (16), 91 (12); Elemental Anal. Calcd (%) for $C_{15}H_{16}BrN$ (290.05): C, 62.08; H, 5.56. Found: C, 62.19; H, 5.59.

***N*-2′,6′-Diisopropylphenyl-2-bromoaniline (1e).** NaO*t*Bu (75 mg, 0.78 mmol), DPPF (23 mg, 7.5 mol%), $Pd_2(dba)_3$ (25 mg, 5.0 mol%) were placed into a dry Schlenk tube. 2,6-Diisopropylaniline (0.1 mL, 0.56 mmol), 1,2-dibromobenzene (0.08 mL, 0.67 mmol), and toluene (2 mL) were added, and the mixture was heated at 100 °C for 14 h. After cooling to room temperature, the mixture was diluted with ether and filtered. The filtrate was concentrated and purified by chromatography on silica gel (0.063−0.100 mm) using 2% Et_2O/hexane as eluant to give 150 mg (80%) **1e** as a colorless viscous oil. ^{1}H NMR ($CDCl_3$): δ 1.11 (d, ^3J = 6.9 Hz, 6H; CH_3), 1.18 (d, ^3J = 6.9 Hz, 6H; CH_3), 3.09 (sep, ^3J = 6.9 Hz, 2H; CH), 5.68 (br s; NH), 6.14 (dd, ^3J = 8.2, ^4J = 1.4 Hz, 1H;

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(26) Heinicke, J.; Nietzschmann, E.; Tzschach, A. *J. Prakt. Chem.* **1983**, *325*, 511–516.

H-6), 6.57 (td, ^3J = 7.8, 7.2, ^4J = 1.4 Hz, 1H; H-4), 7.00 (td, ^3J = 8.2, 7.2, ^4J = 1.3 Hz, 1H; H-5), 7.23 (m, 2H; H-*m*), 7.32 (m, 1H; H-*p*), 7.47 (dd, ^3J = 7.9, ^4J = 1.4 Hz, 1H; H-3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.98 (CH_3), 24.63 (CH_3), 28.30 (CH), 108.82 (C_q-2), 112.60 (CH-6), 118.24 (CH-4), 123.93 (2CH-*m*), 127.74 (CH-*p*), 128.24 (CH-5), 132.31 (CH-3), 134.63 (C_q-*i*), 144.88 (C*q*-1), 147.69 (2 C-*o*); MS Calcd for $C_{18}H_{22}BrN$: 333.1 (^{81}Br), 331.1 (^{79}Br), found (EI, 70 eV, 20 °C): *m*/*z* (%) = 334 (3) [M^++1], 333 (30) [M^+ for ^{81}Br], 332 (4), 331 (29) [M^+ for ^{79}Br], 252 (99), 162 (100).

2-(2-Bromoanilino)pyridine (1f). A Schlenk tube was charged with NaO*t*Bu (143 mg, 1.48 mmol), DPPF (58 mg, 10 mol%), $Pd_2(dba)_3$ (48 mg, 5 mol%), 2-aminopyridine (100 mg, 1.06 mmol), 1,2-dibromobenzene (0.15 mL, 1.27 mmol), and toluene (3 mL), and this mixture was heated at 100 °C for 14 h. After cooling to room temperature, diethyl ether was added, the mixture was filtered, the filtrate was concentrated, and the product was purified by chromatography on silical gel (0.063−0.100 mm) using 10% EtOAc/hexane as eluant to give 247 mg (94%) **1f** as a pale-yellow oil. The NMR data are in accordance with reported values.[16] MS Calcd for $C_{11}H_9BrN_2$: 250.0 (^{81}Br), 248.0 (^{79}Br), found (EI, 70 eV): *m*/*z* (%) = 250 (7) [M^+], 248 (8) [M^+], 169 (100).

(2-Methylaminophenyl)phosphonic Acid Diethyl Ester (2a). (a) General Procedure for Coupling with Diethyl Phosphite. *N*-Methyl-2-bromoaniline (**1a**) (1.18−6.45 mmol) was dissolved in toluene (ca. 70 mL). $Pd(PPh_3)_4$ (4 mol%) and triethylamine (1.6 mmol) or the given amount (Table 2) of phosphane ligand, $Pd_2(dba)_3$, and finally NaO*t*Bu was added, and the mixture was heated at 120 °C for 12 h unless indicated otherwise. Then insoluble material was filtered off, the solution was concentrated and the product **2a** purified by column chromatography on silica gel using 5% ethyl acetate/hexane; yields see Table 2.

(b) Example for Larger Scale Coupling with Diethyl Phosphite. 1a (5.0 g, 26.8 mmol), P(*o*-Tol)$_3$ (490 mg, 6.0 mol%), NaO*t*Bu (3.0 g, 32.2 mmol), $Pd_2(dba)_3$ (490 mg, 2.0 mol%), and diethyl phosphite (4.1 mL, 32.2 mmol) were placed into an oven-dried Schlenk tube. Toluene (ca. 70 mL) was added, the mixture was stirred at 120 °C for 2 d and then filtered. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel (0.063−0.100 mm), using 5% ethyl acetate/hexane providing 3.3 g (50%) **2a** as a pale-yellow oil. The NMR data of **2a** are in accordance with reported values.[10a] Calcd for [M+H$^+$] ($C_{11}H_{18}NO_3P$): 244.10971. HRMS (ESI): Found 244.1097.

2-(2,2-Dimethylpropylamino)phenylphosphonic Acid Diethylester (2b). P(OEt)$_3$ (0.4 mL, 2.27 mmol) was added to **1b** (500 mg, 2.06 mmol) and $Pd(OAc)_2$ (20 mg, 4.0 mol%), and the mixture was heated at 200 °C for 1 h. Then, the product was extracted by the addition of diethyl ether and filtration through celite. The filtrate was concentrated, and the crude product was purified using column chromatography on silica gel, eluant 5% ethyl acetate/hexane, to give 475 mg (77%) **2b** as a colorless oil. ^1H NMR ($CDCl_3$): δ 1.04 (s, 9H; CH_3), 1.32 (t, ^3J = 7.1 Hz, 6H; CH_3), 2.90 (br s, 2H; NCH_2), 4.09 (m, 2H; OCH_2), 6.60−6.72 [3H: vbr s, NH, 6.61 (superimposed ddd, ^3J = 8.3, $^4J_{(P,H)}$ = 3.3, J = 0.8 Hz; H-3), 6.65 (t br, ^3J = 7.6−7.7 Hz; H-5)], 7.33 (tt, ^3J = 8.4, 7.2, ^4J = 1.7, $^5J_{(P,H)}$ = 1 Hz, 1H; H-4), 7.46 (ddd, $^3J_{(P,H)}$ = 14.9, ^3J = 7.6, ^4J = 1.7 Hz, 1H; H-6); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.29 (d, ^3J = 6.6 Hz; OCH_2CH_3), 27.74 (s; CMe_3), 31.74 (s; *C*Me$_3$), 56.07 (s; NCH_2), 62.09 (d, ^2J = 5.1 Hz; OCH_2), 108.35 (d, ^1J = 182.6 Hz; C-1), 111.92 (d, ^3J = 12.1 Hz; C-3), 116.06 (d, ^3J = 14.1 Hz; C-5), 133.58 (d, ^2J = 7.1 Hz; C-6), 134.28 (d, ^4J = 2.1 Hz; C-4), 151.46 (d, ^2J = 8.9 Hz; C_q-2); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.26; MS (EI, 70 eV, 90 °C): *m*/*z* (%) = 299 (11) [M^+], 243 (17), 242 (100), 214 (17), 186 (50), 184 (29), 168 (21); Elemental analysis Calcd (%) for $C_{15}H_{26}NO_3P$ (299.35): C, 60.18; H, 8.75; N, 4.68. Found: C, 60.04; H, 8.90; N, 5.04.

[2-(Adamant-1-ylamino)-phenyl]-phosphonic Acid Diethyl Ester (2c). P(OEt)$_3$ (0.17 mL, 1.02 mmol) was added to **1c** (285 mg, 0.93 mmol) and $Pd(OAc)_2$ (8 mg, 4 mol%), placed into a round-bottomed flask connected to a distillation condenser, and the mixture was heated at 200 °C for 1 h. A small stream of argon was necessary to ensure removal of ethyl bromide and avoid any competing Arbuzov reaction. The product was purified by chromatography on silica gel (0.063−0.100 mm) using 14% EtOAc/hexane as eluant to give 320 mg (94%) colorless solid **2c**, mp = 89−90 °C; ^1H NMR ($CDCl_3$): δ 1.32 (t, ^3J = 7.1 Hz, 6H; CH_3), 1.70 (br t, ^3J = 3.0 Hz, 6H; CH_2), 2.02 (br d, ^3J = 2.4 Hz, 6H; CH_2), 2.12 (br s, 3H; CH), 3.96−4.18 (m, 4H; OCH_2), 6.44 (br s; NH), 6.60 (br m, 1H; H-3), 6.97 (br t, ^3J = 7.7 Hz, 1H; H-5), 7.26 (br t, ^3J = 7.7, 7.3 Hz, 1H; H-4), 7.47 (ddd, $^3J_{(P,H)}$ = 15.0, ^3J = 7.7, ^4J = 1.4 Hz, 1H; H-6); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.31 (d, ^3J = 6.7 Hz; CH_3), 29.69 (s; CH), 36.51 (s; CH_2), 42.70 (s; CH_2), 51.92 (s; NC_q), 61.92 (d, ^2J = 4.7 Hz; OCH_2), 109.34 (d, ^1J = 183.6 Hz; C_q-1), 114.95, 115.10 (2 br s; CH-3, CH-5), 133.21 (d, ^4J = 1.9 Hz; CH-4), 134.10 (d, ^2J = 7.3 Hz; CH-6), 150.96 (d, ^2J = 5.9 Hz; C_q-2); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.54; MS (EI, 70 eV, 170 °C): *m*/*z* (%): 364 (24) [M^++1], 363 (97) [M^+], 307 (20), 306 (100) [M^+-57]; HRMS (ESI) Calcd for [M+H$^+$] ($C_{20}H_{31}NO_3P$): 364.20361; found 364.20356.

2-Mesitylaminophenylphosphonic Acid Diethyl Ester (2d). P(OEt)$_3$ (0.85 mL, 4.94 mmol) was added to **1d** (1.3 g, 4.49 mmol) and $Pd(OAc)_2$ (20 mg, 4 mol%), and the mixture was heated at 200 °C for 4 h as described for **2c**. After cooling, diethyl ether was added, the mixture was filtered through celite, the filtrate was concentrated, and the crude product was purified by column chromatography (silica gel 0.063−0.100 mm) using 10% ethyl acetate/hexane as eluant. The resulting pale-yellow oil crystallized after 1 day at room temperature to give 655 mg (42%) white solid **2d**, mp = 56.5 °C; ^1H NMR ($CDCl_3$): δ 1.36 (t, ^3J = 7.1 Hz, 6H; CH_3), 2.16 (s, 6H; *o*-CH_3), 2.30 (s, 3H; *p*-CH_3), 4.05−4.27 (m, 4H; OCH_2), 6.17 (t br, $^3J \approx {}^4J_{(P,H)}$ = 8.4, 6.6 Hz, 1H; H-3), 6.67 (t, ^3J = 7.6, 7.2, $^4J_{(P,H)}$ = 3.3 Hz, 1H; H-5), 6.94 (s, 2H; *m*-H), 7.18 (tt, ^3J = 8.4, 7.2, ^4J = 1.6, J = 1 Hz, 1H; H-4), 7.53 (ddd, $^3J_{(P,H)}$ = 14.6, ^3J = 7.7, ^4J = 1.6 Hz, 1H; H-6), 7.87 (br s, 1H; NH); $^{13}C\{^1H\}$ (DEPT135) NMR ($CDCl_3$): δ 16.34 (d, ^3J = 6.7 Hz; CH_3), 18.17 (s; *o*-CH_3), 20.94 (s; *p*-CH_3), 62.06 (d, ^2J = 4.8 Hz; OCH_2), 107.79 (d, ^1J = 183.0 Hz; C_q-1), 112.12 (d, ^3J = 11.8 Hz; CH-3), 116.12 (d, ^3J = 14.0 Hz; CH-5), 129.16 (s; 2 CH-*m*), 133.49 (d, ^2J = 7.3 Hz; CH-6), 134.00 (d, ^4J = 2.4 Hz; CH-4), 134.84 (s; C_q-*p*), 135.80 (s; C_q-*i*), 136.28 (s; 2 C_q-*o*), 150.68 (d, ^2J = 8.6 Hz; C_q-2); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.27; MS (EI, 70 eV, 20 °C): *m*/*z* (%) = 348 (16), 347 (100) [M^+], 210 (18), 209 (16), 208 (37), 120 (26). Elemental Anal. Calcd (%) for $C_{19}H_{26}NO_3P$ (347.39): C, 65.69; H, 7.54; N, 4.03. Found C, 65.75; H, 8.15; N, 3.95.

[2-(2,6-Diisopropyl-phenylamino)-phenyl]phosphonic Acid Diethyl Ester (2e). P(OEt)$_3$ (0.062 mL, 0.36 mmol) was added to **1e** (110 mg, 0.33 mmol) and $Pd(OAc)_2$ (3 mg, 4.0 mol%) and as reported for **2b** this mixture was heated at 200 °C for 1 h. The product was purified by chromatography on silica gel (0.063−0.100 mm) using 20% EtOAc/hexane as eluant to give 100 mg (77%) **2e** as a colorless viscous oil. ^1H NMR ($CDCl_3$): δ 1.11 (d, ^3J = 6.9 Hz, 6H; CH_3), 1.17 (d, ^3J = 6.9 Hz, 6H; CH_3), 1.37 (t, ^3J = 7.1 Hz, 6H; OCH_2CH_3), 3.15 (sep, ^3J = 6.9 Hz, 2H; CH), 4.08−4.26 (m, 4H; OCH_2), 6.16 (t br, ^3J = 8.4, $^4J_{(P,H)}$ = 7.1 Hz, 1H; H-3), 6.66 (tdd, ^3J = 7.7, 7.2, $^4J_{(P,H)}$ = 3.3, ^4J = 1.0 Hz, 1H; H-5), 7.17 (tm, ^3J = 8.4, 7.2 Hz, 1H; H-4), 7.21 (m, 2H; H-*m*), 7.30 (m, ^3J = 6.3 Hz, 1H; H-*p*), 7.54 (ddd, $^3J_{(P,H)}$ = 15.0, ^3J = 7.7, ^4J = 1.6 Hz,

1H; H-6), 7.88 (br s; NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.29 (d, ^3J = 6.4 Hz; OCH_2CH_3), 22.94 (s; CH_3), 24.48 (s; CH_3), 28.35 (s; CH), 62.02 (d, ^2J = 5.1 Hz; OCH_2), 107.32 (d, ^1J = 183.3 Hz; C_q-1), 112.31 (d, ^3J = 12.0 Hz; CH-3), 116.02 (d, ^3J = 14.5 Hz; CH-5), 123.84 (s; 2CH-*m*), 127.41 (s; CH-*p*), 133.40 (d, ^4J = 7.9 Hz; CH-6), 133.89 (d, ^2J = 2.4 Hz; CH-4), 134.64 (s; C_q-*i*), 147.43 (s; 2C_q-*o*), 151.88 (d, ^2J = 7.9 Hz; C_q-2); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.33. Calcd for $C_{22}H_{32}NO_3P$, [M+H$^+$] 390.21926, [M+Na$^+$] 412.20120. HRMS (ESI) found for [M+H$^+$] 390.21952, [M+Na$^+$] 412.20118. MS (EI, 70 eV): *m*/*z* (%) = 390 (25) [M^++1], 389 (100) [M^+], 236 (53), 162 (20).

[2-(Pyrid-2′-yl-amino)phenyl]phosphonic Acid Diethyl Ester (2f). 1f (1.5 g, 6.04 mmol) and $Pd(OAc)_2$ (67 mg, 5 mol%) were placed into a round-bottomed flask connected to a distillation condenser. To this, 0.1 mL of a total of 1.14 mL (6.65 mmol) of $P(OEt)_3$ was initially added. The remaining $P(OEt)_3$ was added in three portions between 160 and 180 °C, and this mixture was heated at 200 °C for 30min. The product was purified by chromatography on silica gel (0.063−0.100 mm) using 40% EtOAc/hexane (few drops of Et_3N added) as eluant to give 867 mg (46%) **2f** as a yellow oil. ^1H NMR ($CDCl_3$): δ 1.31 (t, ^3J = 7.1 Hz, 6H; CH_3), 4.00−4.22 (m, 4H; OCH_2), 6.75−6.82 (2H superimposed): 6.78 (ddd, ^3J = 7.3, 4.9, ^4J = 0.8 Hz; H-5′), 6.80 (d br, $^3J \approx$ 8.1 Hz; H-3′), 6.96 (tdd, ^3J = 7.5, 7.2, $^4J_{(P,H)}$ = 3.1, ^4J = 1.0 Hz, 1H; H-5), 7.45−7.63 (3H; superimposed): 7.50 (t br, ^3J = 7−8 Hz, H-4), 7.52 (td, ^3J = 8.2, 7.2, ^4J = 1.9 Hz; H-4′), 7.58 (ddd, $^3J_{(P,H)}$ = 14.7, ^3J = 7.7, ^4J = 1.7 Hz; H-6), 8.25(dd, ^3J = 4.9, ^4J = 1.3 Hz, 1H;H-6′), 8.59 (t, $^3J \approx {}^4J_{PH}$, $^3J+{}^4J$ = 15.3 Hz, 1H; H-3), 9.58 (br s; NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.24 (d, ^3J = 6.7 Hz; OCH_2CH_3), 62.40 (d, ^2J = 5.1 Hz; OCH_2), 112.18 (s; CH-3′), 112.2 (d, ^1J = 181 Hz; C_q-1), 115.67 (s; CH-5′), 118.78 (d, ^3J = 11.3 Hz; CH-3), 120.08 (d, ^3J = 13.8 Hz; CH-5), 132.95 (d, ^4J = 6.5 Hz; CH-6), 133.79 (d, ^2J = 2.3 Hz; CH-4), 137.45 (s; CH-4′), 145.59 (d, ^2J = 7.6 Hz; C_q-2), 147.53 (s; CH-6′), 155.13 (s; C_q-2′); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.21; Calcd for $C_{15}H_{19}N_2O_3P$ (306.3), [M+H$^+$] 307.12061. HRMS (ESI) found for [M+H$^+$] 307.12054. MS found (EI, 70 eV): *m*/*z*(%) = 307 (5) [M^++1], 306 (28) [M^+], 277 (2.4), 249 (2), 305 (12), 233 (7), 231 (11), 168.8 (100).

***N*-Methyl-2-phosphanylaniline (3a). 2a** (3.3 g, 13.5 mmol) was added dropwise at 0 °C to $LiAlH_4$ tablets (1.5 g, 40.7 mmol) stirred in ether (50 mL). The reaction mixture was stirred at room temperature for 2 days. Then degassed water was added dropwise until the evolution of H_2 gas ceased. The solids were filtered off and washed thoroughly with ether. The filtrate was dried over Na_2SO_4 and concentrated in vacuum to give a brown liquid (1.8 g, 94%). This crude **3a** was NMR-spectroscopically pure enough to proceed without further purification directly to the synthesis of **5a**. The NMR data are in accordance with known values.[14]

***N*-2′,2′-Dimethylpropyl-2-phosphanylaniline (3b). 2b** (1.0 g, 3.34 mmol) was added dropwise at 0 °C to $LiAlH_4$ tablets (380 mg, 10.0 mmol) in diethyl ether (20 mL). After stirring at room temperature for 1 day, degassed water was added dropwise until the evolution of H_2 gas ceased. The solid was filtered off and washed thoroughly with ether (3 × 20 mL), the filtrate was dried over Na_2SO_4, and solvent was removed in vacuum to give 564 mg (86%) **3b** as a colorless liquid contaminated by traces of two other phosphanes (δ^{31}P −98.85, −95.55). It was used to synthesize **5b** without further purification. ^1H NMR ($CDCl_3$): δ 1.04 (s, 9H; CH_3), 2.96 (s, 2H; NCH_2), 3.56 (d, ^1J = 199.4 Hz, 2H; PH_2), 4.10 (vbr s; NH), 6.62, 6.63 (superimposed d, t, 2H; H-6, H-4), 7.27 (t br, ^3J = 7.6 Hz, 1H; H-5), 7.48 (ddd, $^3J_{(P,H)}$ = 12.8, ^3J = 7.6, ^4J = 1.7 Hz, 1H; H-3); $^{13}C\{^1H\}$ (DEPT135) NMR ($CDCl_3$): δ 27.74 (s; CMe_3), 31.81 (s; *C*Me_3), 55.66 (s; NCH_2), 109.56 (d, ^3J = 1.5 Hz; CH-6), 110.17 (d, ^1J = 10.7 Hz; C_q-2), 116.28 (d, ^3J = 12.7 Hz; CH-4), 131.45 (d, ^4J = 1.1 Hz; CH-5), 138.28 (d, ^2J = 35.1 Hz; CH-3), 151.02 (s; C_q-1); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −154.59; MS (EI, 70 eV, 20 °C): *m*/*z* (%) = 196 (7) [M^++1], 195 (51) [M^+], 138 (100) [M^+-*t*Bu], 136 (39), 106 (25). HRMS (ESI in MeOH, NH_4OAc): Calcd for [M+H]$^+$ $C_{11}H_{19}NP$ 196.12496, found 196.12496.

***N*-Adamant-1′-yl-2-phosphanylaniline (3c).** A solution of **2c** (188 mg, 0.51 mmol) in diethyl ether (2 mL) was added dropwise to $LiAlH_4$ (59 mg, 1.55 mmol) and stirred in diethyl ether (2 mL) in an ice-bath. After stirring at room temperature for 2 days, degassed water was added dropwise until the evolution of H_2 gas ceased. The insoluble compounds were separated by filtration and washed thoroughly with ether, and the organic layer was dried over Na_2SO_4, filtered, and concentrated to give 85 mg of a colorless solid (63%), mp = 110−111 °C; ^1H NMR ($CDCl_3$): δ 1.71 (br d, ^3J = 2.8 Hz, 6H; CH_2), 2.00 (br d, ^3J = 3.0 Hz, 6H; CH_2), 2.14 (br s, 3H; CH), 3.60 (d, $^1J_{(P,H)}$ = 200.9 Hz; PH_2), 4.05 (br s; NH), 6.65 (tm, ^3J = 7.4, 7.1, $^4J+{}^4J_{(P,H)}$ = 2.0 Hz, 1H; H-4), 7.00 (dm, ^3J = 8.3, $^4J+{}^4J_{(P,H)}$ = 2.7 Hz, 1H; H-6), 7.20 (tm, ^3J = 8.3, 7.3, ^4J = 1.2 Hz, 1H; H-5), 7.49 (ddd, $^3J_{(P,H)}$ = 11.9, ^3J = 7.4, ^4J = 1.6 Hz, 1H; H-3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.74 (s; CH), 36.47 (s; CH_2), 43.18 (s; CH_2), 52.63 (s; NC_q), 113.32 (d, ^1J = 9.8 Hz; C_q-2), 115.42 (s; CH-6), 117.23 (d, ^3J = 11.1 Hz; CH-4), 130.48 (s; CH-5), 138.37 (d, ^2J = 30.4 Hz; CH-3), 149.21 (s; C_q-1); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −147.58 (tiny impurities by phosphanes δ −153.3, −88.3); MS (EI, 70 eV, 180 °C): *m*/*z* (%) = 259 (12) [M^+], 202 (4), 147 (4), 136 (12), 135 (100). HRMS (EI, 70 eV): Calcd for $C_{16}H_{22}NP$ 259.1490, found 259.1483.

***N*-Mesityl-2-phosphanylaniline (3d).** A solution of **2d** (4.3 g, 12.3 mmol) in diethyl ether (20 mL) was added dropwise during 20 min to $LiAlH_4$ tablets (1.4 g, 37.1 mmol) stirred in ether (40 mL) in an ice-bath. After stirring for 1 day at room temperature, degassed water was added dropwise until the evolution of H_2 gas stopped. Solids were filtered off and washed thoroughly with ether (3 × 20 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed in vacuum to give 2.9 g (96%) of a colorless solid, mp = 60 °C; ^1H NMR ($CDCl_3$): δ 2.15 (s, 6H; *o*-CH_3), 2.31 (s, 3H; *p*-CH_3), 3.75 (d, $^1J_{(P,H)}$ = 200.4 Hz, 2H; PH_2), 5.41 (br s, 1H; NH), 6.14 (dt, ^3J = 8.2, $^4J+{}^4J_{(P,H)}$ = 2.9 Hz, 1H; H-6), 6.68 (tt, ^3J = 7.4, $^4J+{}^4J_{(P,H)}$ = 2.4 Hz, 1H; H-4), 6.95 (s, 2H; H-*m*), 7.11 (td, ^3J = 7.8, ^4J = 1.6 Hz, 1H; H-5), 7.53 (ddd, $^3J_{(P,H)}$ = 11.9, ^3J = 7.4, ^4J = 1.6 Hz, 1H; H-3); $^{13}C\{^1H\}$ (DEPT135) NMR ($CDCl_3$): δ 18.14 (s; *o*-CH_3), 20.94 (s; *p*-CH_3), 110.79 (d, ^1J = 10.2 Hz; C_q-2), 111.32 (d, ^3J = 1.6 Hz; CH-6), 117.63 (d, ^3J = 11.4 Hz; CH-4), 129.26 (s; 2CH-*m*), 131.17 (s; CH-5), 135.45, 135.80 (2 s; C_q-*i*, C_q-*p*), 135.96 (s; C_q-*o*), 138.04 (d, ^2J = 31.8 Hz; CH-3), 149.13 (d, ^2J = 1.1 Hz; C_q-1); ^{31}P NMR ($CDCl_3$): δ −152.01; MS (EI, 70 eV, 20 °C): *m*/*z* (%) = 244 (7) [M+H$^+$], 243 (54) [M^+], 228 (12), 226 (18), 211 (15), 123 (100), 113 (6); HRMS (EI, 70 eV): Calcd for $C_{15}H_{18}NP$ 243.1177 (100), found 243.1165.

***N*-2′,6′-Diisopropylphenyl-2-phosphanylaniline (3e).** A solution of **2e** (385 mg, 0.98 mmol) in diethyl ether (2 mL) was added dropwise at 0 °C to $LiAlH_4$ (112 mg, 2.96 mmol) in diethyl ether (5 mL). After stirring at room temperature for 2 days and workup as described for **3a**, 230 mg (82%) **3e** were obtained as a colorless viscous oil, containing a small amount of phosphane impurities. It was used to synthesize **5e** without purification. ^1H NMR (C_6D_6): δ 1.05 (d, ^3J = 6.9 Hz, 6H; CH_3), 1.12 (d, ^3J = 6.9 Hz, 6H; CH_3), 3.16 (sep, ^3J = 6.9 Hz, 2H; CH), 3.60 (d, $^1J_{(P,H)}$ = 198.1 Hz, 2H; PH_2), 5.48 (br s; NH), 6.24 (dt, ^3J = 8.2, $^4J+{}^4J_{(P,H)}$ = 2.7 Hz, 1H; H-6), 6.58 (tt, ^3J = 7.4, 7.3, $^4J+{}^4J_{(P,H)}$ = 2.4 Hz, 1H; H-4), 6.95 (t,

^3J = 8.5, 7.4, ^4J = 1.4 Hz, 1H; H-5), 7.18 (m; 2H-*m*), 7.24 (m; 1H-*p*), 7.52 (ddd, $^3J_{(P,H)}$ = 12.2, ^3J = 7.5, ^4J = 1.3 Hz, 1H; H-3); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 23.83 (s; CH_3), 25.42 (s; CH_3), 29.36 (s; CH), 111.04 (d, ^1J = 11.0 Hz; C_q-2), 112.51 (d, ^3J = 1.2 Hz; CH-6), 118.85 (d, ^3J = 12.1 Hz; CH-4), 124.99 (s; 2CH-*m*), 128.72 (s; CH-*p*), 132.28 (s; CH-5), 136.42 (s; C_q-*i*), 139.30 (d, ^2J = 33.3 Hz; CH-3), 148.21 (s; 2C_q-*o*), 151.75 (s; C_q-1); $^{31}P\{^1H\}$ NMR(C_6D_6): δ −154.64 (small phosphane impurity δ −89.0); MS (EI, 70 eV, 20 °C): *m*/*z* (%) = 286 (3) [M^++1], 285 (28) [M^+], 257 (24), 242 (100), 198 (20), 84 (84); HRMS (EI, 70 eV): Calcd for $C_{18}H_{24}NP$ 285.1646, found 285.1650.

***N*-Pyrid-2′-yl-2-Phosphanylaniline (3f).** A solution of **2f** (350 mg, 1.14 mmol) in diethyl ether (2 mL) was added dropwise at 0 °C to $LiAlH_4$ (130 mg, 3.42 mmol) in diethyl ether (15 mL). After stirring at room temperature for 1 day, degassed water was added dropwise until the evolution of H_2 gas ceased. Solids were separated by filtration and washed thoroughly with ether. The organic layer was dried over Na_2SO_4 and was filtered and concentrated to give 216 mg (93%) of a yellow viscous oil, which solidified at room temperature in few hours, mp = 48−52 °C. It was slightly contaminated but was used for synthesis of **5f** without further purification. ^1H NMR ($CDCl_3$): δ 3.60 (d, $^1J_{(P,H)}$ = 202.3 Hz, 2H; PH_2), 6.31 (dt, ^3J = 8.3, $^4J \approx J_{(P,H)}$ = 0.8 Hz, 1H; H-3′), 6.35 (ddd, ^3J = 7.2, 4.9, ^4J = 0.8 Hz, 1H; H-5′), 6.79 (tt, ^3J = 7.7, 7.2, $^4J \approx J_{(P,H)}$ = 1.1 Hz, 1H; H-4), 6.94 (td, ^3J = 8.3, 7.2, ^4J = 1.9 Hz, 1H; H-4′), 7.05 (tm, J = 7.7, ^4J+$^5J_{(P,H)}$ = 1.8 Hz, 1H; H-5), 7.18 (br s; NH), 7.37 (td, $^3J_{(P,H)}$ = 8.8, ^3J = 7.2, ^4J = 1.2 Hz, 1H; H-3), 7.50 (ddd, ^3J = 8.1, $^4J_{(P,H)}$ = 2.5, ^4J = 1.1 Hz, 1H; H-6), 8.18 (ddd, ^3J = 5.0, J = 1.9, $J_{(P,H)}$ = 0.8 Hz, 1H; H-6′); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 108.99 (s; CH-3′), 115.76 (s; CH-5′), 123.88 (d, ^3J = 1.0 Hz; CH-6), 124.23 (d, ^1J = 11.0 Hz; C_q-2), 124.78 (d, ^3J = 6.6 Hz; CH-4), 130.83 (s; CH-5), 137.65 (d, ^2J = 18.4 Hz; CH-3), 138.15 (s; CH-4′), 144.55 (d, ^2J = 6.9 Hz; C_q-1), 149.54 (s; CH-6′), 157.70 (s; C_q-2′); $^{31}P\{^1H\}$ NMR($CDCl_3$): δ −141.04 (small phosphane impurity δ −83.74); MS (EI, 70 eV, 100 °C): *m*/*z* (%) = 203 (2) [M^++1], 202 (19) [M^+], 201 (12), 169 (12), 108 (11), 84 (100), 56 (20); HRMS (EI, 70 eV): Calcd for $C_{11}H_{11}N_2P$ 202.06544, found 202.06485.

1-Methyl-1H-1,3-benzazaphosphole (5a). 3a (1.17 g, 8.40 mmol) and dimethylformamide dimethyl acetal (DMFA) (1.23 mL, 9.25 mmol) were heated at 40 °C for 2 d. Then excess DMFA was removed in vacuum. The residue was diluted with Et_2O, basic impurities were extracted with degassed 10% aqueous H_2SO_4 (at room temperature), and the ether layer was washed with degassed water and dried over Na_2SO_4. Removal of the solvent gave 1.06 g (85%) spectroscopically pure **5a**. The NMR data are in accordance with known values.[9]

1-(2′,2′-Dimethylpropyl)-1H-1,3-benzazaphosphole (5b) and Intermediate 4b. DMFA (0.31 mL, 2.34 mmol) was added to crude **3b** (458 mg, 2.34 mmol). After stirring for 24 h at 20 °C, NMR control spectra showed formation of **4b** and **5b** in a 2−3:1 molar ratio. The mixture was then heated at 40 °C for 2 d. Work-up as described for **5a** furnished 380 mg (79%) **5b** as a white solid, mp = 82−83 °C. Single crystals of **5b** were grown from a concentrated hexane solution at room temperature; for crystal data, see Table 3. ^1H NMR ($CDCl_3$): δ 1.01 (s, 9H; CMe_3), 4.10 (s, 2H;, NCH_2), 7.15 (tdd, ^3J = 7.0, J = 2.0, 1.0 Hz, 1H; H-5), 7.36 (tt, ^3J = 8.4, 7.0, ^4J+$^5J_{(P,H)}$ = 2.3 Hz, 1H; H-6), 7.60 (dm, ^3J = 8.5 Hz, 1H; H-7), 8.07 (ddm, ^3J = 7.8, $^3J_{(P,H)}$ = 4.2, ^4J = 1.2, ^5J = 0.7 Hz, 1H; H-4), 8.44 (d, $^2J_{(P,H)}$ = 38.1 Hz, 1H; H-2); $^{13}C\{^1H\}$ (DEPT135) NMR ($CDCl_3$): δ 28.34 (s; CH_3), 34.59 (d, ^4J = 1.3 Hz; *C*Me_3), 60.91 (d, ^3J = 2.4 Hz; NCH_2), 113.43 (s; CH-7), 119.68 (d, ^3J = 11.8 Hz; CH-5), 124.28 (d, ^4J = 2.6 Hz; H-6), 129.31 (d, ^2J = 21.4 Hz; CH-4), 141.79 (d, ^1J = 39.8 Hz; C_q-3a), 143.43 (d, ^2J = 6.0 Hz; C_q-7a), 163.02 (d, ^1J = 52.0 Hz; C_q-2); ^{31}P NMR ($CDCl_3$): δ 70.8 (dd, $^2J_{(P,H)}$ = 38, $^2J_{(P,H)}$ = 3−4 Hz); MS (EI, 70 eV, 20 °C): *m*/*z* (%) = 206 (10) [M+1$^+$], 205 (85) [M^+], 148 (43), 147 (100), 135 (23), 106 (16), 77 (15); Elemental analysis Calcd (%) for $C_{12}H_{16}NP$ (205.10): C, 70.23; H, 7.86; N, 6.82. Found: C, 69.66; H, 7.87; N, 6.63. *Intermediate* **4b**: ^1H NMR ($CDCl_3$): δ 1.00 (s; CMe_3), 2.91 (d, ^3J = 5.7 Hz; NCH_2), 3.03 (d, $^4J_{(P,H)}$ = 3.3 Hz; NMe_2), 4.70 (br s; NH), 6.54 (dd, ^3J = 8.1, $^4J_{(P,H)}$ = 3.0 Hz; H-6), 6.59 (dd, ^3J = 7.4, ^4J = 1.0 Hz; H-4), 7.12 (td, ^3J = 8.0, 7.6, ^4J = 1.6 Hz; H-5), 7.32 (ddd, ^3J = 7.5, $^3J_{(P,H)}$ = 6, ^4J = 1.6 Hz; H-3), 8.78 (d, ^2J = 14.1 Hz; *E*-P=CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.8.

1-(Adamant-1′-yl)-1H-1,3-benzazaphosphole (5c). 3c (70 mg, 0.26 mmol) and DMFA (40 μL, 0.29 mmol) was stirred at 60 °C for 7 d. ^{31}P NMR control of the crude product displayed a strong signal for **5c** and minor signals for **4c** (δ 39.9) and other byproduct (δ −30.9, −55.3, −76.3, −75.5). The reaction mixture was diluted with diethyl ether, and *N*-basic impurities were extracted with air-free cold 10% aqueous H_2SO_4. The ether layer was washed with degassed water, dried over Na_2SO_4, and filtered. Removal of solvent in vacuum gave 50 mg (69%) colorless solid, mp = 160−162 °C. ^1H NMR ($CDCl_3$): δ 1.85 (br d, ^3J = 2.7 Hz, 6H; CH_2), 2.33 (br s, 3H; CH), 2.48 (br d, ^3J = 3.3 Hz, 6H; CH_2), 7.13 (tm, ^3J = 7.7, 7.0, $^4J_{(P,H)}$ = 1.7, ^4J = 0.9 Hz, 1H; H-5), 7.32 (tt, ^3J = 8.4, 7.0, ^4J+$^5J_{(P,H)}$ = 2.5 Hz, 1H; H-6), 8.08 (superimp. d, ^3J = 8.2 Hz, 1H; H-7), 8.10 (superimp. tm, ^3J = 7.7, $^3J_{(P,H)}$ = 5.2 Hz, 1H; H-4), 8.80 (d, ^2J = 38.1 Hz, 1H; H-2); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.07 (s; CH), 36.27 (s; CH_2), 41.71 (s; CH_2), 61.28 (d, ^3J = 2.9 Hz, NC_q), 117.18 (s; CH-7), 119.51 (d, ^3J = 12.3 Hz; CH-5), 123.26 (d, ^4J = 2.4 Hz; CH-6), 130.15 (d, ^2J = 22.4 Hz; CH-4), 141.59 (d, ^2J = 5.4 Hz; C_q-7a), 144.64 (d, ^1J = 36.5 Hz; C_q-3a), 157.47 (d, ^1J = 49.8 Hz; CH-2); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 66.4; HRMS (ESI): Calcd for [M+H$^+$] $C_{17}H_{21}NP$ 270.14061, found 270.14078.

1-Mesityl-1H-1,3-benzazaphosphole (5d) and Intermediate 4d. 3d (2.8 g, 11.5 mmol) and DMFA (1.68 mL, 12.6 mmol) was stirred at 40 °C until the cyclization was complete (10 d, NMR control). The reaction mixture was diluted with diethyl ether and extracted with air-free cold 10% aqueous H_2SO_4. The ether layer was washed with degassed water, dried over Na_2SO_4, and filtered. Removal of solvent in vacuum gave 2.8 g (96%) **5d** as a colorless viscous oil, which solidified at 4 °C, mp = 55−56 °C; ^1H NMR ($CDCl_3$): δ 1.82 (s, 6H; *o*-CH_3), 2.39 (s, 3H; *p*-CH_3), 7.01 (dm, ^3J = 7.0, ^4J = 1.3 Hz, 1H; H-7), 7.03 (s, 2H-*m*), 7.19 (tdd, ^3J = 8.0, 7.0, J = 2.0, ^4J = 1.2 Hz, 1H; H-5), 7.28 (tt, ^3J = 8.2, 7.0, $^4J \approx ^5J_{(P,H)}$ = 1.3, 1 Hz, 1H; H-6), 8.14 (dddd, ^3J = 7.7, $^3J_{(P,H)}$ = 3.9, ^4J = 1.3, ^5J = 0.7 Hz, 1H; H-4), 8.41 (d, $^2J_{(P,H)}$ = 38.7 Hz, 1H; H-2); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.07 (s; *o*-CH_3), 21.10 (s; *p*-CH_3), 113.19 (s; CH-7), 120.26 (d, ^3J = 11.5 Hz; CH-5), 125.02 (d, ^4J = 2.8 Hz; CH-6), 129.21 (d, ^2J = 20.6 Hz; CH-4), 129.23 (s; 2CH-*m*), 136.07 (s; 2C_q-*o*), 136.23 (d, ^3J = 2.4 Hz; C_q-*i*), 138.83 (s; C_q-*p*), 141.24 (d, ^1J = 41.9 Hz; C_q-3a), 142.85 (d, ^2J = 6.4 Hz; C_q-7a), 161.43 (d, ^1J = 54.2 Hz; CH-2); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.1 (trace −32.8); HRMS (EI, 70 eV): Calcd for $C_{16}H_{16}NP$ 253.1020, found 253.1023. *Intermediate* **4d**: ^1H NMR ($CDCl_3$): δ 2.17 (s; *o*-Me), 2.30 (s; *p*-Me), 3.07 (d, $^4J_{(P,H)}$ = 3.0 Hz; NMe_2), 5.99 (d br, $^4J_{(P,H)}$ = 4.4 Hz; NH), 6.06 (dd, ^3J = 8.1, $^4J_{(P,H)}$ = 2.8, ^4J = 1.1 Hz; H-6), 6.65 (td, ^3J = 7.3, ^4J = 1.1 Hz; H-4), 6.99 (td, ^3J = 8.1, 7.3, ^4J = 1.5 Hz; H-5), 7.39 (ddd, ^3J = 7.3, $^3J_{(P,H)}$ = 6, ^4J = 1.5 Hz, H-3), 8.90 (d, ^2J = 14.0 Hz, *E*-P=CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.2.

1-(2′,6′-Diisopropylphenyl)-1H-1,3-benzazaphosphole (5e) and Intermediate 4e. 3e (1.0 g, 3.50 mmol) and DMFA (0.51 mL, 3.85 mmol) was stirred at 60 °C. NMR control showed unconverted

4e even after 10 days. An equimolar amount of aqueous HCl was added, and stirring was continued for 3 days at 60 °C. Then the reaction mixture was diluted with diethyl ether and extracted with air-free cold 10% aqueous H_2SO_4. The ether layer was washed with degassed water, dried over Na_2SO_4, and filtered. Removal of solvent in vacuum gave 1.0 g of a yellowish gummy solid, which according to ^{31}P NMR was impure benzazaphosphole. This was distilled in a short-column distillation device at 10^{-4} Torr/60 °C (bath temperature) to give 600 mg (58%) **5e** as a colorless viscous oil. ^{1}H NMR ($CDCl_3$): δ 0.98 (d, ^3J = 6.9 Hz, 6H; CH_3), 1.09 (d, ^3J = 6.9 Hz, 6H; CH_3), 2.08 (sep, ^3J = 6.9 Hz, 2H; CH), 7.01 (dm, ^3J = 8.2, ^4J = 1.9, 1.2 Hz, 1H; H-7), 7.20 (tdd, ^3J = 8.0, 7.0, $^4J_{(P,H)}$ = 2.0, ^4J = 1.2 Hz, 1H; H-5), 7.28 (tm, ^3J = 8.2, 7.0, ^4J = 1.3 Hz, 1H; H-6), 7.32 (d br, ^3J = 7.8 Hz, 2H; H-*m*), 7.51 (dd, ^3J = 7.6, 7.3 Hz, 1H, H-*p*), 8.15 (dddd, ^3J = 7.6, $^3J_{(P,H)}$ = 3.8, ^4J = 1.2−1.5, ^5J = 0.7−0.9 Hz, 1H; H-4), 8.42 (d, $^2J_{(P,H)}$ = 38.5 Hz, 1H; H-2); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.76 (s; CH_3), 24.90 (s; CH_3), 28.22 (s; CH), 113.76 (s; CH-7), 120.38 (d, ^3J = 11.5 Hz; CH-5), 124.28 (s; 2CH-*m*), 125.00 (d, ^4J = 2.6 Hz; CH-6), 129.10 (d, ^2J = 20.8 Hz, CH-4), 129.88 (s; CH-*p*), 135.95 (d, ^3J = 2.5 Hz, Cq-*i*), 140.94 (d, ^1J = 41.7 Hz; C_q-3a), 144.36 (d, ^2J = 6.7 Hz; C_q-7a), 147.11 (s; 2 C_q-*o*), 162.53 (d, ^1J = 54.4 Hz; CH-2); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 76.0; MS (EI, 70 eV): *m*/*z* (%) = 296 (9) [M^++1], 295 (54) [M^+], 252 (100); HRMS (EI, 70 eV): calcd for $C_{19}H_{22}NP$ 295.1490, found 295.1492. *Intermediate* **4e**: ^{1}H NMR ($CDCl_3$): δ 1.10 (d,^3J = 6.9 Hz, 6H; CH_3), 1.16 (d, ^3J = 6.9 Hz, 6H; CH_3), 3.08 (d, $^4J_{(P,H)}$ = 3.3 Hz; NMe_2), 3.17 (sep, ^3J = 6.9 Hz, 2H; CH), 6.05 (dq, ^3J = 8.1, $^4J_{(P,H)}$ = 2.6, ^4J = 1.2 Hz; H-6), 6.63 (td, ^3J = 7.2, ^4J = 1.0 Hz; H-4), 6.97 (td, ^3J = 7.8, ^4J = 1.5 Hz; H-5), 7.23−7.45 (m, 4H; 2H-*m*, 1H-*p*, H-3), 8.91 (d, ^2J = 13.9 Hz; *E*-P=CH), NH superimposed; ^{31}P{^{1}H} NMR: δ 42.00 ($CDCl_3$); 46.4 (C_6D_6).

1-(Pyrid-2′-yl)-1H-1,3-benzazaphosphole (5f). 3f (200 mg, 0.989 mmol) and dimethyl formamide dimethyl acetal (0.14 mL, 1.08 mmol) were stirred at 60 °C. After 7 days, the cyclization was complete (NMR control). Distillation in a short-column distillation device at 2×10^{-6} Torr 100 °C (bath temperature) gave 100 mg (48%) of a pale-yellow oil consisting mainly of **5f**, contaminated by ca. 13 mol% of an unidentified phosphane. ^{1}H NMR ($CDCl_3$): δ 7.25 (tdd, ^3J = 7.9, 7.2, $^4J_{(P,H)}$ = 1.9, ^4J = 1.0 Hz, 1H; H-5), 7.35 (ddd, ^3J = 7.4, 4.9, ^4J = 1.0 Hz, 1H; H-5′), 7.39 (tt, ^3J = 8.4, 7.2, ^4J+$^5J_{(P,H)}$ = 2.5 Hz, 1H; H-6), 7.54 (dt, ^3J = 8.1, ^4J = 1.0, ^5J = 0.7 Hz, 1H; H-3′), 7.91 (td, ^3J = 7.5, 8.1, ^4J = 1.9 Hz, 1H; H-4′), 8.02 (dq, ^3J = 8.5, $^4J_{(P,H)}$ = 1.7, ^4J = 1.0 Hz, 1H; H-7), 8.12 (ddd, ^3J = 7.8, $^3J_{(P,H)}$ = 4.4, ^4J+^5J = 1.6 Hz, 1H; H-4), 8.66 (ddd, ^3J = 4.9, ^4J = 1.9, ^5J = 0.8 Hz, 1H; H-6′), 8.93 (d, $^2J_{(P,H)}$ = 37.4 Hz, 1H, H-2); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 85.0, impurity −58.2 (intensity ratio 87:13%); MS (EI, 70 eV, 65 °C): *m*/*z* (%) = 213 (16) [M^++1], 212 (100) [M^+], 211 (15), 185 (13), 167 (12), 106 (15), 78 (24); HRMS (ESI in MeOH, NH_4OAc): Calcd for [M+H]$^+$ $C_{12}H_{10}N_2P$ 213.05761, found 213.05762.

2-Di(*tert*-butyl)phosphanyl-1-methyl-1H-1,3-benzazaphosphole (7a). 5a (300 mg, 2.01 mmol) was dissolved in THF (5 mL). This was cooled to −78 °C and KO*t*Bu (368 mg, 3.01 mmol) was added. Then, *t*BuLi (1.61 mL, 2.41 mmol) was added dropwise to the formed yellow solution at the same temperature. This mixture was stirred for 6 h while slowly warming to −30 °C. The reaction mixture was again cooled to −78 °C and after addition of excess tBu$_2$PCl (0.96 mL, 5.02 mmol) stirred overnight at room temperature. THF was removed from the reaction mixture, and the residue was extracted with hexane. The solvent was removed in vacuum, and the remaining product was distilled in a microdistillation device at 10^{-6} Torr, 45 °C bath temperature to give colorless oily **7a**, which crystallized after short time, yield 177 mg (30%). ^{1}H NMR (C_6D_6): δ 1.27 (d, $^3J_{(P,H)}$ = 12.4 Hz, 18H; $PCMe_3$), 3.81 (dd, $^4J_{(P,H)}$ = 2.1, 0.6 Hz, 3H; NMe), 7.06−7.21 (m, 1H; aryl), 7.19−7.30 (m, 2H; aryl), 8.14 (dddd, ^3J = 7.9, $^3J_{(P,H)}$ = 3.7, $^4J \approx {}^5J_{(P,H)}$ = 1.0 Hz, 1H; H-4); ^{13}C{^{1}H} (DEPT135) NMR (THF-d_8): δ 30.70 (dd, ^2J = 15.4, ^4J = 5.6 Hz; C*Me*$_3$), 33.36 (dd, ^1J = 19.6, ^3J = 2.6 Hz; *C*Me$_3$), 33.83 (s; NMe), 114.24 (d, ^3J = 2.6 Hz; CH-7), 120.70 (d, ^3J = 11.8 Hz; CH-5), 125.46 (d, ^4J = 2.8 Hz; CH-6), 128.71 (d, ^2J = 20.0 Hz; CH-4), 143.53 (d, ^1J = 43.9 Hz; C_q-3a), 146.00 (dd, ^2J+^3J = 6.6 Hz; C_q-7a), 173.23 (dd, ^1J = 80.2, 29.9 Hz; C_q-2); ^{31}P{^{1}H} NMR (C_6D_6): δ 16.1 (d, ^2J = 17.9 Hz), 110.9 (d, ^2J = 17.9 Hz); HRMS (EI, 70 eV): Calcd for $C_{16}H_{25}NP_2$ 293.1453, found 293.1462.

2-Di(*tert*-butyl)phosphanyl-1-neopentyl-1H-1,3-benzazaphosphole (7b). KO*t*Bu (471 mg, 3.86 mmol) was added to a solution of **5b** (792 mg, 3.86 mmol) in THF (10 mL) at −78 °C followed by the dropwise addition of *t*BuLi solution (3.09 mL, 4.63 mmol, 1.5 M in pentane). This mixture was stirred for 6 h, while slowly warming up to −40 °C. The yellow reaction mixture was again cooled to −78 °C, and after dropwise addition of excess tBu$_2$PCl (1.54 mL, 8.11 mmol) it was stirred overnight at room temperature. THF was removed from the reaction mixture in vacuum, and the residue was extracted with hexane. NMR control in C_6D_6 revealed **7b** contaminated only by unconverted tBu$_2$PCl. The product was then distilled in a microdistillation device at a bp of 30−31 °C/10^{-5} Torr (bath 65 °C) to give 741 mg (55%) colorless microcrystals, including some small single crystals suitable for crystal structure determination (crystal data, Table 3). ^{1}H NMR (C_6D_6): δ 0.93 (s, 9H; CMe_3), 1.08 (d, $^3J_{(P,H)}$ = 12.0 Hz, 18H; $PCMe_3$), 3.87 (vbr; NCH_A), 5.37 (vbr; NCH_B), 7.06 (tq, ^3J = 7.8, 6.9, ^4J+$^4J_{(P,H)}$+$^6J_{(P,H)}$ = 2.6 Hz, 1H; H-5), 7.20 (tt, ^3J = 8.5, 6.9, ^4J+$^4J_{(P,H)}$ = 2.5 Hz, 1H; H-6), 7.51 (d unresolved q, ^3J = 8.6 Hz, 1H; H-7), 8.12 (qq, ^3J = 7.8, $^3J_{(P,H)}$ = 4.0, ^4J = 1.3, ^5J = 0.7 Hz, 1H; H-4); ^{13}C{^{1}H} (DEPT135) NMR (C_6D_6): δ 28.53 (d, ^2J = 17.1 Hz; C*Me*$_3$), 30.65 (d, ^5J = 4.1 Hz; C*Me*$_3$), 36.24 (br unresolved τ, P*C*Me$_3$), 36.45 (τ, $|^4J$+$^4J'|$ = 3.0 Hz; *C*Me$_3$), 57.42 (dd, $^{3(2P)}J$ = 19.4, ^3J = 3.6 Hz; NCH_2), 116.57 (d, ^3J = 2.1 Hz; CH-7), 120.95 (d, ^3J = 11.6 Hz; CH-5), 124.97 (d, ^4J = 2.9 Hz; CH-6), 129.41 (d, ^2J = 20.6 Hz; CH-4), 144.17 (d, ^1J = 42.8 Hz; C_q-3a), 146.75 (dd, ^2J = 4.3, ^3J = 1.7 Hz; C_q-7a), 175.05 (dd, ^1J = 79.4, $^{1(2P)}J$ = 34.5 Hz; C_q-2); ^{31}P{^{1}H} NMR (C_6D_6): δ 20.03, 114.84 (2d, $^2J_{(P,P)}$ = 17.2 Hz); HRMS Calcd for $C_{20}H_{33}NP_2$ 349.20882, found 349.20878.

Lithiation of 5c and Reaction with tBu$_2$PCl. 5c (40 mg, 0.148 mmol) in Et_2O (1 mL)/THF (1 mL) was lithiated with *t*BuLi (0.10 mL, 0.178 mmol) at −60 °C and slow warming to 10 °C over 5 h. Then, tBu$_2$PCl (30 μL, 0.163 mmol) was added at −60 °C. Stirring overnight at 20 °C, removal of the solvent in vacuum and extraction of the residue with diethyl ether furnished a yellow oil, according to ^{31}P NMR (C_6D_6) control containing unconverted tBu$_2$PCl (δ 147.1, $I_{rel.}$ 61), addition products (δ −21.9, $I_{rel.}$ 12), (δ −16.0, $I_{rel.}$ 4), diphosphane **11c** (δ −8.3, 51.1, $J_{(P,P)}$ = 8.7 Hz, I_{rel} each 12), tBu$_4$P$_2$ (δ 40.2, trace), **7c** (δ 31.1, 133.2, $J_{(P,P)}$ = 10.8 Hz, $I_{rel.}$ each 3), and unconverted **5c** (δ 69.2, I_{rel} 7). (The ^{31}P relative intensities refer to an acquisition time of 0.655 s and delay D1 of 2.00 s.) Because of the small phosphorus signals, no efforts were made to separate **7c**. The assignment of the two doublets is based on the good accordance with the characteristic chemical shift values and $^2J_{(P,P)}$ coupling constants of **7a**,**b** and **7d**.

2-Di(*tert*-butyl)phosphanyl-1-mesityl-1H-1,3-benzazaphosphole (7d). Reaction of *t*BuLi (in pentane, 1.54 mL, 2.27 mmol) with **5d** (480 mg, 1.89 mmol) in THF (3 mL) at −60 to −10 °C over 4 h gave a yellow-orange solution of **6d**. After cooling to −60 °C, tBu$_2$PCl (0.37 mL, 1.96 mmol) was added dropwise. The mixture was stirred at room temperature overnight. THF was

removed in vacuum, the residue was extracted with diethyl ether, and the solution was concentrated yielding yellow oily **7d**, slightly contaminated by **5d** and byproduct with δ^{31}P −3.23, −32.80. Dissolution of this oil in a small amount of THF and overlayering with *n*-hexane gave 460 mg (61%) of soft colorless crystals of **7d**, which were unsuitable for X-ray structure determination because of weak diffraction. Repeated crystallization attempts with the mother liquor led to a few smaller crystals that proved to be the hitherto unknown (tBu$_2$PHO·LiCl)$_4$. This was presumably formed from tBu$_2$PCl, traces of moisture and LiCl dissolved in THF (crystal data, Table 3). **7d**: ^{1}H NMR ($CDCl_3$): δ 1.26 (d, $^3J_{(P,H)} = 12.0$ Hz, 18H; CMe_3), 1.75 (s, 6H; *o*-CH_3), 2.37 (s, 3H; *p*-CH_3), 6.83 (dq, $^3J = 8.1$, $^4J+^5J+J = 3.2$ Hz, 1H; H-7), 6.98 (d, $J = 0.6$ Hz, 2H; H-*m*), 7.16 (tt, $^3J = 7.7$, 6.9, $^4J+J = 3.2$ Hz, 1H; H-5), 7.22 (tt, $^3J = 8.2$, 6.9, $^4J+J = 2.8$ Hz, 1H; H-6), 8.12 (dddd, $^3J = 7.6$, $^3J_{(P,H)} = 3.5$, $^4J = 1.3$, $J = 0.7$ Hz, 1H; H-4); ^{13}C{^{1}H} (DEPT135) NMR ($CDCl_3$): δ 19.08 (d, $^5J = 3.9$ Hz; *o*-CH_3), 21.18 (s; *p*-CH_3), 31.13 (dd, $^2J = 14.6$, $^4J = 5.3$ Hz; C*Me*$_3$), 33.22 (dd, $^1J = 20.7$, $^3J = 2.8$ Hz; *C*$_q$Me$_3$), 114.73 (d, $^3J = 2.0$ Hz; CH-7), 120.18 (d, $^3J = 11.3$ Hz; CH-5), 125.20 (d, $^4J = 3.0$ Hz; CH-6), 128.13 (d, $^2J = 19.2$ Hz; CH-4), 129.09 (s; 2CH-*m*), 135.86 (t, $^3J = 2.7$ Hz; C$_q$-*i*), 136.53 (d, $^4J = 1.5$ Hz; 2C$_q$-*o*), 138.34 (s; C$_q$-*p*), 142.30 (dd, $^1J = 44.5$, $^3J = 1.1$ Hz; C$_q$-3a), 145.37 (dd, $^2J = 5.1$, $^3J = 3.2$ Hz; C$_q$-7a), 173.66 (dd, $^1J = 82.0$, $^{1(2P)}J = 36.7$ Hz, C$_q$-2); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 22.0 (d, $^2J = 19.2$ Hz), 121.2 (d, $^2J = 19.2$ Hz); MS (EI, 70 eV, 340 °C): *m*/*z* (%) = 398 (1) [M^++1], 397 (8) [M^+], 341 (18), 284 (46), 252 (21), 57 (100); HRMS calcd for $C_{24}H_{33}NP_2$ 397.2088, found 397.2083. **(tBu$_2$PHO·LiCl)$_4$:** ^{1}H NMR (THF, $CDCl_3$): δ 1.27 (d, $^3J_{(P,H)} = 15.0$ Hz; $PCMe_3$), 6.08 (d, $^1J_{(P,H)} = 429$ Hz; PH); ^{31}P NMR (THF, $CDCl_3$): δ 65.7.

3-*tert*-Butyl-1-mesityl-2,3-dihydro-1H-1,3-benzazaphosphole (10d) as Major Product. tBuLi (0.13 mL, 0.191 mmol, 1.5 M in pentane) was added dropwise to **5d** (44 mg, 0.173 mmol) in diethyl ether (1 mL) at −60 °C. The mixture was slowly warmed to room temperature and stirred overnight. Removal of solvent in vacuum gave a yellow solid, which in THF-d_8 solution displayed four ^{31}P signals at δ −6.59 (**9d**), −3.92 (**10d**), −2.62 (**9d′**), 113.93 (**6d**), relative intensity 25:50:8:17 (acquisition time 0.655 s, delay 2.00 s). Methanolysis by two drops of CH_3OH and repeated ^{31}P NMR measurement revealed signals at δ −3.90 (**10d**) and 78.75 (**5d**) (relative intensity 82:18; molar ratio by ^{1}H integration 73:27%). **10d:** ^{1}H NMR (THF-d_8): δ 1.03 (d, $^3J_{(P,H)} = 12.1$ Hz, 9H; CMe_3), 1.85 (s, 3H; *p*-CH_3), 2.21 (s, 3H; *o*-CH_3), 2.26 (s, 3H; *o*-CH_3), 3.59 (dd, $^2J_{(P,H)} = 24.3$, $^2J = 13.0$ Hz, 1H; PCH_{trans}), 3.87 (dd, $^2J = 13.0$, $^2J_{(P,H)} = 4.0$ Hz, 1H; PCH_{cis}), 5.81 (d br, $^3J = 7.9$ Hz, 1H; H-7), 6.56 (tdd, $^3J = 7.4$, $^4J_{(P,H)} = 2.5$, $^4J = 0.9$ Hz, 1H; H-5), 6.90 (s br, 1H; H-*m*), 6.96 (s and td superimposed, $^3J = 7.7$, $^4J = 1.4$ Hz, 3H; H-*m* and H-6), 7.31 (ddd, $^3J = 7.3$, $^3J_{(P,H)} = 5.0$, $^4J = 1.3$ Hz, 1H; H-4); ^{13}C{^{1}H} NMR (THF-d_8): δ 18.31 (*o*-CH_3), 18.88 (*o*-CH_3), 20.91 (*p*-CH_3), 26.82 (d, $^2J = 15.3$ Hz; C*Me*$_3$), 30.44 (d, $^1J = 20.0$ Hz; *C*$_q$Me$_3$), 48.20 (d, $^1J = 24.3$ Hz; PCH_2N), 108.14 (CH-7), 117.05 (d, $^3J = 7.1$ Hz; CH-5), 123.19 (d, $^1J = 14.4$ Hz; C$_q$-3a), 130.05 (CH-6), 130.96, 131.10 (2s; 2CH-*m*), 132.33 (d, $^2J = 20.9$ Hz; CH-4), 137.49, 137.53, 138.54, 139.16 (2 C$_q$-*o*, C$_q$-*i*, C$_q$-*p*), 155.66 (d, $^2J = 1.1$ Hz; C$_q$-**7a**).

Lithiation of 5e and Reaction with tBu$_2$PCl. 5e (193 mg, 0.653 mmol) in THF (2 mL) was lithiated with tBuLi (0.42 mL, 0.718 mmol) at −60 °C and slowly warmed to 10 °C over 8 h. tBu$_2$PCl (0.14 mL, 0.718 mmol) was added dropwise at −60 °C. Stirring overnight at 20 °C, removal of THF in vacuum, and extraction of the residue with diethyl ether furnished a yellow oil. ^{31}P NMR (C_6D_6) control indicated a large amount of unconverted tBu$_2$PCl (δ 147.1, I_{rel} 54), a smaller amount of **10e** (δ −3.0, I_{rel} 9) and a new compound (δ −37.2, I_{rel} 15), tBu$_4$P$_2$ (δ 40.2, I_{rel} 7), and small amounts of **7e** (δ 20.2, 125.5, $J = 18.2$ Hz, I_{rel} 13 for each doublet) and a species with δ 62.5 (I_{rel} 2). (Relative intensities refer to an acquisition time 0.655 s and delay 2.0 s.) MS (EI, 70 eV, 160 °C): *m*/*z* (%) = 439 (2) [M^+, **7e**], 353 (54) [M^+, **10e**], 297 (100) [**10e**$^+$-C_4H_8]. No efforts were made to separate **7e**.

3-*tert*-Butyl-1-(2′,6′-diisopropylphenyl)-2,3-dihydro-1H-1,3-benzazaphosphole (10e) as Major Product. tBuLi in pentane (0.37 mL, 0.629 mmol) was added to **5e** (155 mg, 0.524 mmol) in Et_2O (2 mL) at −60 °C and stirred overnight. Replacement of ether by THF-d_8 and ^{31}P NMR control displayed a major peak at δ −3.4, a trace peak at δ 13.49 and a minor peak at δ 111.18 (**6e**, I_{rel} 25% at AQ 0.33 s, D1 2.0 s). The PCH_2N signal in the ^{13}C NMR spectrum indicated the protonated form **10e**. ^{13}C{^{1}H} (DEPT135) NMR (THF-d_8), **10e**: δ 26.82 (d, $^2J = 15.4$ Hz; P*CMe*$_3$), 30.42 (d, $^1J = 20.3$ Hz; P*C*Me$_3$), 24.45, 24.60, 24.67, 24.85 (CH_3), 28.73, 28.98 (CH), 51.12 (d, $^1J = 25$ Hz; PCH_2N), 109.02 (CH-7), 117.19 (d, $^3J = 7.0$ Hz; CH-5), 123.10 (d, $^1J = 14.2$ Hz; C$_q$-3a), 123.89, 124.63 (2CH-*m*), 129.05 (CH-*p*), 130.72 (CH-6), 132.50 (d, $^2J = 21.0$ Hz, CH-4), 139.48 (C$_q$-*i*), 149.17, 149.54 (2CH-*o*), 157.04 (d, $^2J = 1.2$ Hz; C$_q$-7a); **6e**: δ 24.02, 24.50 (CH_3), 28.25 (CH), 112.73 (CH-7), 117.07 (d, $^3J = 6.3$ Hz; CH-5), 119.19 (CH-6), 126.19 (d, $^2J = 11.5$ Hz; CH-4), 126.40 (2CH-*m*), 127.51 (CH-*p*), 144.48 (C$_q$-*i*, uncertain), 147.68 (2CH-*o*), 148.47 (d, $^1J = 63.6$ Hz; C$_q$−3a), 150.62 (d, $^2J = 7.9$ Hz, C$_q$−**7a**); doublet of C$_q$−2(Li) in noise. (The assignment is based on the higher intensity signals of **10e** compared to **6e** and similar chemical shifts and P−C coupling constants of relative carbon nuclei in **10e** and **10c** and in **6e** and **6a**,[9] respectively.)

Crystal Structure Analysis of 5b, 7b, and (tBu$_2$PHO·LiCl)$_4$. Data Collection. For **5b**, data were recorded on a Bruker SMART 1000 CCD diffractometer using monochromated Mo Kα radiation; for **7b** on an Oxford Diffraction Nova O diffractometer with monochromated Cu Kα radiation and for the lithium compound on a Bruker SMART 6000 CCD diffractometer using monochromated Cu Kα radiation. The copper data were corrected for absorption (multiscan method). *Structure refinement*: The structures were refined anisotropically on F^2 using the program *SHELXL-97*.[27] Hydrogen atoms were refined using rigid methyl groups or a riding model. Crystal data are presented in Table 3.

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Supporting Information Available: Procedures for lithiation of **5b** in THF and in pentane without additive, observation of complex formation of **7b** with $[RhCl(COD)]_2$, example for use of **7b** in the Suzuki-coupling of phenylboronic acid with 2-bromopyridine, table of selected NMR data of **5**−**7**, crystallographic data of CIF files of **5b**, **7b**, and (tBu$_2$PHO·LiCl)$_4$, ^{13}C and/or ^{31}P NMR spectra of the compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) *SHELXL-97, A Program for Refining Crystal Structures*; Sheldrick, G. M., Ed.; University of Göttingen: Göttingen, Germany, 1997.