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Sterically and Polarity-Controlled Reactions of *t*BuLi with P=CH-NR Heterocycles: Novel Heterocyclic P- and P,O-Ligands and Preliminary Tests in Transition-Metal Catalysis

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Abstract: (1*R*)-1,3-Benzazaphospholes **1a**–**c**, P=CH-NR heterocycles of the indole type, react with *t*BuLi in two ways, depending on the steric demand of the *N*-substituent and the polarity of the medium. The presence of small *N*-alkyl groups induces CH-deprotonation in the 2-position to give hetaryllithium reagents **2a** and **2b**, whereas bulky *N*-substituents and nonpolar solvents change the reactivity towards addition at the P=C bond. The preferred regioselectivity is *tert*-butylation at phosphorus, occurring with excellent diastereoselectivity for *trans*-adducts **3b** and **3c**, but the inverse *tert*-butylation at C2 to **5b** was also observed. *N*-Neopentyl groups, with intermediate steric demand, give rise to formation of mixtures in ethers but allow switching either to selective CH lithiation in THF/KO*t*Bu or to addition in pentane. Bulkier *N*-adamantyl groups always cause preferred addition. Protonation, silylation, and carboxylation were used to convert the P=CLi-NR, (*E*)-*t*BuP-CHLi-NR, and LiP-CH(*t*Bu)-NR species into the corresponding σ^2-P or σ^3-P compounds **4b** and **6a**,**b**, **7b**,**c**, or **8b**–**10b** with additional N and/or O donor sites. Slow diffusion-controlled air oxidation of **10b** led to the *meso*-diphosphine **11b**. Preferred η^1-P coordination was shown for an [Rh(cod)Cl] complex **12b**, and the potential of the new ligands **4b** and **7b** in catalysis was demonstrated by examples of Pd-catalyzed C–N coupling and Ni-catalyzed ethylene oligomerization (TON > 6300). Crystal structures of **6b**, **11b**, and **12b** are presented.

Keywords: homogeneous catalysis · nickel · oligomerization · phosphorus · rhodium

Introduction

Trivalent phosphorus compounds have found extensive application in coordination chemistry and catalysis and cover a wide range of ligand types and properties,[1] from highly basic and bulky donor phosphanes to π-acidic two-coordinated phosphenes, bisphosphenes, or phosphaaromatics.[2] The latter class have so far found less application than phosphanes, but there are promising studies of the use of two-coordinated phosphorus compounds, and in particular of functionally substituted derivatives as hybrid ligands, in coordination chemistry and catalysis.[2,3] Furthermore, stable P=C compounds possess broad but so far largely unexplored potential for the synthesis of novel phosphane ligands. A recently highlighted example is the anionic polymerization of $MesP{=}CPh_2$ and copolymerization with styrene[4] to produce novel multiphosphane materials. It is based on addition of organolithium species at the phosphorus-carbon double bond, which has also been reported for other types of P=C compounds.[5] In continuation of our research on carbo- and heterocyclically anellated azaphospholes and azaphospholides,[6,7] we have observed competition between addition of *tert*-butyllithium at the double bond of the P=CH-NR group and CH-lithiation with bulky *N*-alkylated 1,3-benzazaphospholes;[8] we report here on sterically and polarity-controlled formation of P=CLi-NR and/or (*E*)-*t*BuP-CHLi-NR species,

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: NMR data for **3b**–**5b**, formed by lithiation of **1b** in THF, tables with detailed X-ray structural data for **6b**, **11b,** and **12b**, ^{13}C NMR spectra of the reported compounds.

their conversion by electrophiles into new σ^2- and σ^3-P hybrid ligands, and preliminary tests of their use in catalysis.

Results and Discussion

Treatment of 1-methyl-1,3-benzazaphosphole (**1a**) with *t*BuLi (pentane) at low temperature in THF or diethyl ether led in good yield to the P=CLi-NMe species **2a** (Scheme 1), which crystallized from THF/hexane as a μ-C bridged dimer with two THF molecules per Li ion. It is stable at room temperature for up to 2 d and was treated with various electrophiles to yield functionally substituted derivatives.[6] It was expected that bulkier *N*-substituents would further increase the stability of related lithiophosphenes and tolerate harsher reaction conditions, thereby extending the scope of coupling reactions. Treatment of the bulkier *N*-neopentyl benzazaphosphole **1b**[8] with *tert*-butyllithium (−60 to 0 °C) and subsequently with carbon dioxide and chlorotrimethylsilane, however, showed more complex behavior. In THF solution, CH-lithiation competes with addition of *t*BuLi at the P=CH substructure, leading to a mixture of **2b**, **3b**, and **5b**, characterized by NMR data (^{31}P, ^{1}H, ^{13}C) and trapping reactions. On treatment with CO_2 and workup by silyl ester formation and methanolysis, **2b** was converted into the σ^2-P-heterocyclic amino acid **6b** (Scheme 1), which behaves like a normal carboxylic acid, is soluble in ether, and forms the well known hydrogen-bonded dimers in the crystal (Figure 1). The lack of zwitterionic properties indicates a low basicity at nitrogen, attributable to inclusion of the nitrogen lone electron pair into the aromatic π system. The yield (30 %) was considerably lower than observed for **6a** from **2a**[6] under equivalent conditions, because of the competing addition of *t*BuLi in the case of **1b**. The primary addition product **3b** was converted into **4b** and into the carboxylation product **7b**, both of which were identified by NMR in the crude product mixture, in good agreement with the NMR data for isolated species obtained by independent synthesis (see below). The formation of the dihydrobenzazaphosphole **4b** from **1b** and *t*BuLi takes place quite rapidly in THF, more slowly (overnight) in diethyl ether, and not at all in pentane, which is consistent with the high reactivity of **3b** and deprotonative attack on **1b** in ethers to give **2b**, or on ethers themselves. The deprotonation of ethers by reactive branched alkyllithium reagents is well known in the literature.[9] The hetaryllithium species **2b**, however, is less reactive and does not attack ethers during its lifetime.

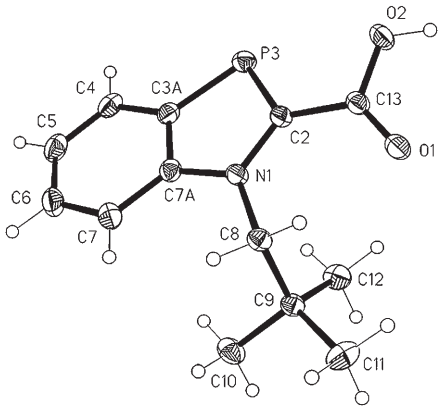
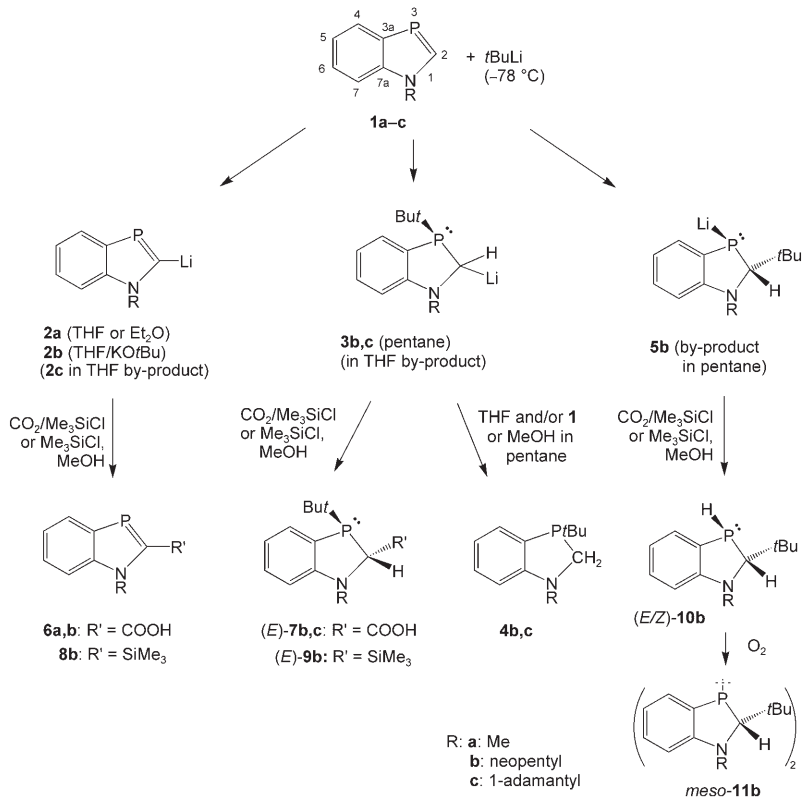


Figure 1. Molecular structure of **6b** in the crystal. Ellipsoids are at 50 % probability. Selected interatomic distances [Å] and angles [°]: P3−C2 1.7255(12), P3−C3A 1.7619(13), N1−C2 1.3798(15), C2−C13 1.4798(17); C2-P3-C3A 88.35(6), N1-C2-P3 115.55(9), C2-N1-C7A 111.22(10), C2-N1-C8 125.48(10); P3-C2-C13-O1 −170.06(10), P3-C2-C13-O2 10.30(15); hydrogen bond O2–H02···O1#1: D–H 0.88(2), H···A 1.76(2), D···A 2.6430(13), ∢(DHA) 174.9(18).



Scheme 1. Sterically and polarity-controlled reactions of *t*BuLi with *N*-alkylbenzazaphospholes and conversion with electrophiles (CO_2/$ClSiMe_3$ or $ClSiMe_3$).

To find out the reason for the unexpected addition of *t*BuLi to the P=C bond of the elec-

tronically highly stabilized ring system, the lithiation of **1b** was performed under varying conditions. When **1b** was treated with one to five equivalents of *t*BuOK and one equivalent of *t*BuLi in THF at −78 °C and excess Me_3SiCl was added to the resulting solution, only 2-(trimethylsilyl)-benzazaphosphole (**8b**) was obtained, along with a small amount of recovered **1b**. Silylated *tert*-butyl-dihydrobenzazaphosphole **9b** could not be detected, even in the crude reaction mixture. This shows that highly polar additives such as KO*t*Bu favor the deprotonation of **1** over addition. The facilitation of deprotonation reactions by Schlosser bases is well known,[10] but the suppression of addition at the P=C bond in this way is novel and surprising, as the high polarity of the metal-carbon bond in a Schlosser reagent should also accelerate addition at P=C.

As a countercheck, the lithiation reaction was performed in the nonpolar solvent *n*-pentane. Quenching by methanolysis provided **4b** and **10b** in a 75:25 molar ratio (by ^{1}H NMR integration of CMe_3 signals), carboxylation followed by silylation and methanolysis led to precipitation of the zwitterionic heterocyclic phosphanyl amino acid (*E*)-**7b** in 68% yield and a small amount of **10b** in the remaining solution, and trimethylsilylation of the primary lithium compounds gave a mixture of **9b** and **10b**. Neither **8b** nor **4b** could be detected in any of these reactions, indicating suppression of CH deprotonation of **1b** by *t*BuLi or **3b**. The major products were the *E* diastereoisomers of **9b**, accompanied by minor amounts of 2-*tert*-butyl-dihydrobenzazaphosphole (**10b**), which was formed as a result of the opposite regioselectivity in the addition step and methanolysis of the P−$SiMe_3$ group in the workup. In this case both pairs of diastereoisomers were detected by ^{1}H and ^{31}P NMR spectra, but the *E* isomers are also favored for steric reasons. The *E*/*Z* assignment of **9b** and **10b** was based on the strong dihedral angle dependence of two-bond ^{31}P–^{1}H coupling constants. If the proton at C2 is in a *trans* position relative to the phosphorus lone electron pair (*E* diastereoisomers) then $^2J_{P,H}$ is small (4.6 and 1.7 Hz for (*E*)-**9b** and (*E*)-**10b**), while if it is in *cis* position (*Z* diastereoisomers) $^2J_{P,H}$ is large.[11] The *E* configuration with oppositely directed axial 2- and 3-substituents, in this case determined by X-ray diffraction, is also manifested in the symmetrical diphosphane *meso*-**11b**, formed as single crystals by slow diffusion-controlled air oxidation of **10b** in methanol (Figure 2).

Since the highly air-sensitive mixture of **9b** and **10b**, synthesized on a small scale, could not be separated in a convenient way, and in order to characterize concomitantly the coordination properties of the ambidentate dihydrobenzazaphospholes with P and N donor sites, the mixture was treated with a semi-equivalent of $[Rh(1,5\text{-cod})Cl]_2$ in THF (Scheme 2). After concentration and overlayering with *n*-hexane, single crystals of the air-stable dihydrobenzazaphosphole-Rh(cod)Cl complex **12b** binding the ligand **9b** were obtained. The crystal structure analysis (Figure 3) showed a racemate with square-planar rhodium and η^1-P coordination of the ligand, without contacts of rhodium to nitrogen. The bond lengths and angles for the Rh(COD)Cl fragment are in the typical range for $Rh(PR_3)(cod)Cl$ complexes.[12] Also typically, the Rh−C bonds *trans* to the phos-

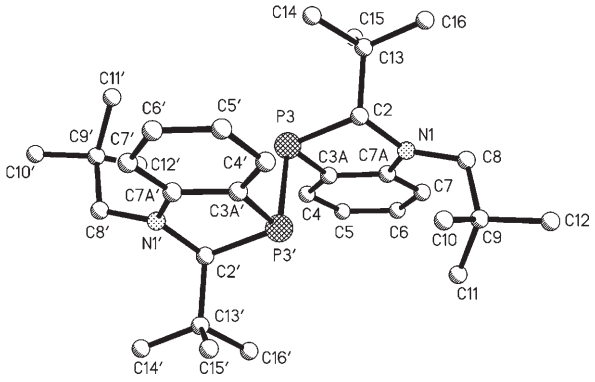
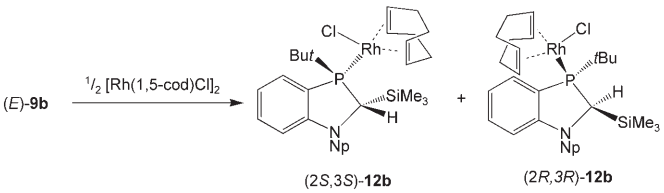


Figure 2. Molecular structure of (2*R*,3*S*,2′*S*,3′*R*)-**11b** in the crystal. Ellipsoids are at 50% probability. Selected interatomic distances [Å] and angles [°]: P3−P3′ 2.2367(4), P3−C2 1.8886(11), P3′−C2′ 1.8838(11), P3−C3A 1.8146(12), P3′−C3A′ 1.8160(12), C2−N1 1.4691(14), C2′−N1′ 1.4694(14), N1−C7A 1.3885(14), N1′−C7A′ 1.3880(14); N1-C2-P3 105.77(7), N1′-C2′-P3′ 106.29(7), C2-P3-C3A 89.10(5), C2′-P3′-C3A′ 89.22(5), C2-P3-P3′ 97.13(4), C3A-P3-P3′ 99.72(4), P3-P3′-C2′ 99.96(4), P3-P3′-C3A′ 95.85(4).



Scheme 2. Structural characterization of (*E*)-**9b** as (*S*,*S*) and (*R*,*R*) enantiomer mixture by diastereoisomeric rhodium complexes **12b**.

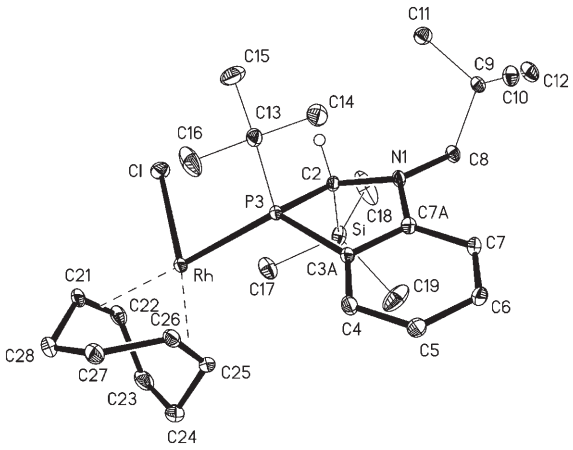


Figure 3. Molecular structure of (2*RS*,3*RS*)-**12b** (the (*S*,*S*) enantiomer is shown). Ellipsoids are at 30% probability. Hydrogen atoms and THF (0.5 THF/(2*RS*,3*RS*)-**12b**) have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: C2−P 1.859(2), P−C3A 1.817(2), P−C13 1.908(2), Si−C2 1.939(2), Rh−P 2.3354(5), Rh−Cl 2.3832(6), Rh−C21 2.218(2), Rh−C22 2.204(2), Rh−C25 2.123(2), Rh−C26 2.116(2), C21−C22 1.377(4), C25−C26 1.393(4), P-C2-N 93.95(6), C3A-P3-C2 89.32(9), P-Rh-C21 162.38(7), P-Rh-C22 161.03(7), P-Rh-C25 96.75(7), P-Rh-C26 93.95(6), P-Rh-Cl 88.47(2).

phane donor atom are longer than those *trans* to chloride and the corresponding C=C distances are shorter and longer, respectively. The relative configuration of the asymmetric carbon and phosphorus atoms in the depicted ligand is (2*S*,3*S*). The (2*R*,3*R*) enantiomer is generated by the inversion symmetry of the space group. The P–C2 bond is, as expected, much longer than P=C in 1*H*-1,3-benzazaphospholes and longer than P–C3A (sp^2 carbon), but considerably shorter than P–C3 to the *tert*-butyl group. Conversely, the C2–Si bond is much longer than the Si–C bonds to the methyl groups. The smallest angle within the five-membered ring is that of C3a-P-C2, followed by P-C2-N. This is in accordance with the lower tendency to hybridization for elements of higher periods.

To find out whether greater steric hindrance can lead to addition even in polar solvents, and also to improved regioselectivity, 1-adamantyl-1,3-benzazaphosphole (**1c**)[8] was treated with *t*BuLi in diethyl ether (−60 to 20 °C, 5 h) and subsequently with CO_2. For easier workup the carboxylate was silylated with Me_3SiCl and the ester was cleaved with methanol. ^{31}P NMR monitoring of the crude product revealed formation of **7c** but neither **6c** nor a secondary phosphane **10c**. Crystallization from CH_2Cl_2/hexane provided microcrystals of the heterocyclic α-phosphanyl amino acid (*E*)-**7c**. The *E* configuration is indicated by the small $^2J_{P,H}$ coupling constant (3.2 Hz). Diastereoisomers of *Z* configuration could not be detected. As the five-membered ring is no longer part of the aromatic system after addition of *t*BuLi at the P=C bond, the nitrogen lone electron pair causes *N*-basicity and a zwitterionic structure in (*E*)-**7b** or (*E*)-**7c**, indicated by a strong downfield shift ($\Delta\delta = 0.8$ to 1.2) of the adjacent CH-2 proton signal relative to those of its counterparts in **4b** and **9b**. Competing protonation at phosphorus cannot be detected by NMR, although *tert*-butyl and *o*-aminoaryl (+M) substituents cause relatively high *P*-basicity. The phosphorus resonance is observed in the usual phosphane region. However, an indirect hint at increased *P*-basicity is given by the high sensitivities of (*E*)-**7b** and (*E*)-**7c** to hydrolysis by water, as observed for acyclic α-phosphanyl amino acids,[13] which gives evidence of the acetal-like nature. In the absence of the COOH group or acid the dihydrobenzazaphospholes are stable to water, like acetals in the presence of tertiary amines. In an early report on dihydrobenzazaphospholes obtained by cyclocondensation of *P*-secondary 2-phosphanylanilines with aldehydes and ketones, sensitivity to hydrolysis was not mentioned.[14]

The *P*-basicity and presence of bulky *P*-*t*Bu substituents in the above adducts suggested that they might be useful ligands in palladium-catalyzed coupling reactions. It is known that aryl aminations (Buchwald–Hartwig aminations),[15] important in view of the large number of bulk and fine chemicals containing aryl amines as substructures,[16] are favored by basic and bulky ligands.[17] The starting materials for the *N*-aryl-1,3-benzazaphospholes[8] and related *N*-aryl-pyrido-1,3-azaphospholes[18] are also synthesized by this coupling. This prompted us to test **4b** in the coupling of 2-bromopyridine with 2,4,6-trimethylaniline in the presence of NaO*t*Bu in toluene (100 °C, 48 h). This reaction, recently reported for catalysis by dppp/$[Pd_2(dba)_3]$,[19] provided *N*-mesityl-2-aminopyridine in 53% yield (after purification) in the presence of 7.5/5 mol% **4b** and $[Pd_2(dba)_3]$. Catalysts formed from **4b** and $Pd(OAc)_2$ (5/5 mol% or 1/2 mol%) gave unsatisfactory levels of conversion (yields after isolation 29 and 13%).

Further catalytic tests were performed with the benzazaphosphole-2-carboxylic acids **6a** and **6b** and the dihydro derivative (*E*)-**7b** because they have a P-CHR-COOH substructure, as did the early $\widehat{PO}^-$–nickel chelate catalysts for the Shell Higher Olefin Process.[20] While solutions of the weakly *P*-basic, rather π-acidic benzazaphospholes[6] **6a** or **6b** and $[Ni(cod)_2]$ were inactive, those with (*E*)-**7b** were highly active. Addition of ethylene to a solution of (*E*)-**7b** and $[Ni(cod)_2]$ (each 65 μmol) in toluene at a starting pressure of ca. 50 bar (12.3 g C_2H_4) and with heating at 70 °C led to efficient oligomerization with >94% conversion of ethylene (TON >6360). The reaction was complete within 1 h, as shown by the pressure–time plot (Figure 4). The reaction at

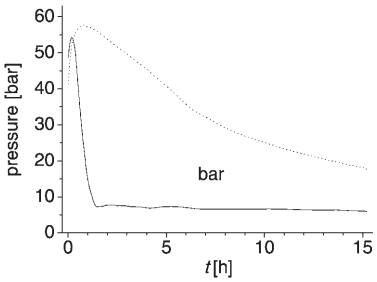


Figure 4. Pressure–time plot for batch polymerization of ethylene in toluene in the presence of **7b**/$[Ni(cod)_2]$ (solid line). The reaction is faster than with 2-diphenylphosphanylphenol/$[Ni(cod)_2]$ (115/106 mmol) at 70 °C (dotted line).[21]

70 °C is faster than the oligomerization in the presence of 2-diphenylphosphanylphenolate/$[Ni(cod)_2]$ catalysts, preferably performed at 80–100 °C,[21], and the average molecular weight is considerably lower. Here, along with a small amount of liquid oligomers, a waxy polymer (m.p. 115–117 °C, M_{NMR} 725, α/internal olefins 78/22%, Me/Vin 1.6/1) was obtained, consisting mainly of linear α-olefins, as is typical for SHOP-type catalysts. This suggests that, as shown for phosphanylacetic acid nickel catalysts,[20] a $\widehat{PO}^-$-chelate structure is formed, stabilizing the catalyst.

Conclusion

In conclusion, we have shown that electron-rich P=CH-NR heterocycles, which, like diagonally related indoles, usually undergo C2 lithiation by *t*BuLi in polar solvents, are driven towards addition at the P=C bond by the presence of bulky *N*-substituents. The reaction of *N*-neopentyl-1,3-benzazaphosphole, occupying an intermediate position and affording a mixture in THF, can be controlled by the polarity of the medium. Addition of KO*t*Bu leads to a strong preference

for CH lithiation, suppressing addition, whereas nonpolar hydrocarbon solvents have the opposite effect, furnishing addition products only, with a preference for *tert*-butylation at phosphorus and high diastereoselectivity for the *trans* adduct in this case. The less favored addition of the *tert*-butyl carbanion at C2 is completely suppressed in the case of the bulkier *N*-1-adamantyl group. Substitution of the benzazaphospholyl- or *P*-*tert*-butyldihydrobenzazaphospholyllithium reagents by electrophiles allows access to novel functionally substituted σ^2- or σ^3-phosphorus compounds. This allows coordination chemical and catalytic studies with novel P=C carboxylic acid derivatives or heterocyclic α-phosphanyl amino acids.

Experimental Section

All reactions were performed under dry nitrogen or argon with use of Schlenk techniques and freshly distilled, ketyl-dried solvents. NMR solvents were dried (C_6D_6 and [D_8]THF over $LiAlH_4$, $CDCl_3$ over P_4O_{10}) and recondensed in vacuum before use. Me_3SiCl was also recondensed in vacuum. The synthesis of **1b** and **1c** has been reported separately.[8] Other chemicals were used as purchased. NMR spectra were recorded on multinuclear FT-NMR ARX 300 or Avance 300 (Bruker) spectrometers at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 MHz (^{31}P). Shift references are tetramethylsilane for ^{1}H and ^{13}C NMR and H_3PO_4 (85%) for ^{31}P NMR. Coupling constants refer to $J_{H,H}$ in ^{1}H NMR and $J_{P,C}$ in ^{13}C NMR data unless stated otherwise. Assignments are supported by additional DEPT measurements. Assignment numbers are given in Scheme 1; selected spectra are found in the Supporting Information. Mass spectra were recorded on an AMD40 (Intectra) single-focusing mass spectrometer. HRMS measurements were carried out in Göttingen with a double focusing sector-field instrument MAT 95 (Finnigan) by EI (70 eV, PFK as reference substances) or by ESI in MeOH, MeOH/NH_4OAc, or MeCN with a 7 T APEX IV Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics). Melting points were determined with a Sanyo Gallenkamp melting point apparatus in capillaries (uncorrected).

Lithiation of 1b in THF: *t*BuLi (1.5 M pentane solution, 0.23 mL, 0.34 mmol) was added dropwise at −60 °C to **1b** (64 mg, 0.31 mmol) in THF (2 mL). This mixture was allowed to warm slowly to −40 °C and stirred for 4 h. The solvent was removed in vacuum to give an orange-yellow crystalline residue. The ^{31}P NMR spectrum showed sharp signals for **2b** ($\delta = 104.3$ ppm) and **4b** ($\delta = -9.1$ ppm) and two small but broad signals in the phosphane and phosphide regions ($\delta = 5.3$, −41.6 ppm), tentatively assigned to **3b** and **5b**; ^{1}H integration of *t*Bu signals (of neopentyl group) ca. 40:28:17:15 (for equal intensity order). Compound **2b**: ^{1}H NMR ([D_8]THF): $\delta = 0.93$ (s; CMe_3), 6.73 (tm, $^3J = 7$–8 Hz, 1H; H-5), 6.92 (td, $^3J = 7$–8, $^4J = 1.6$ Hz, 1H; H-6), 7.38 (d, $^3J = 8.2$ Hz, 1H; H-7), 7.62 ppm (dt, $^3J = 7.6$, $^4J \approx {}^3J_{P,H} \approx 1.5$ Hz, 1H; H-4); ^{13}C{^{1}H} (DEPT) NMR ([D_8]THF): $\delta = 29.66$ (CMe_3), 35.47 (CMe_3), 65.10 (d, $^3J = 7.3$ Hz; NCH_2), 112.75 (d, $^3J = 1.3$ Hz; CH-7), 116.15 (d, $^3J = 6.4$ Hz; CH-5), 118.47 (CH-6), 126.39 (d, $^2J = 12.2$ Hz; CH-4), 149.44 (d, $^2J = 8.9$ Hz; C_q-7a), 150.03 (d, $^1J = 60.5$ Hz; C_q-3a), 253.11 ppm (d, $^1J = 109.9$ Hz; C_{Li}-2). These NMR data, except for those relating to the different *N*-substituent, are closely similar to those of pure **2a**, characterized unambiguously by X-ray crystallography as the μ-CLi-bridged dimer with two THF molecules per lithium.[6] Data for **4b** are in good accordance with those of independently synthesized **4b** recorded in C_6D_6 (see below).

1-(2,2-Dimethylpropyl)-1*H*-1,3-benzazaphosphole-2-carboxylic acid (6b): *t*BuLi (1.7 M in pentane, 0.75 mL, 1.27 mmol) was added dropwise at −60 °C to **1b** (217 mg, 1.05 mmol) in THF (3 mL). This mixture was allowed to warm slowly to 0 °C over 5 h. The resulting orange-yellow solution was cooled to −60 °C, and excess CO_2 gas was passed through the solution for 1 h (color change to yellow). The mixture was stirred at room temperature overnight and was then cooled to −60 °C, and Me_3SiCl (0.16 mL, 1.27 mmol) was added dropwise. After the system had warmed to room temperature (2 h), THF was evaporated in vacuum, excess dry MeOH (8 mL) was added, and after the system had been stirred for 2 h, methanol and Me_3SiOMe were removed in vacuum. The residue was extracted with diethyl ether, and the ether layer was washed twice with degassed aqueous H_2SO_4 (10%). The ether layer was then washed with de-

Table 1. Crystallographic data.

	6b	**11b**	**12b**
empirical formula	$C_{13}H_{16}NO_2P$	$C_{32}H_{50}N_2P_2$	$C_{29}H_{50}ClNO_{0.5}PRhSi$
formula weight	249.24	524.68	618.12
T [K]	133(2)	100(2)	133(2)
λ [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
unit cell dimensions			
a [Å]	5.8021(4)	13.4813(3)	9.4178(6)
b [Å]	13.0437(8)	13.8134(3)	36.045(2)
c [Å]	16.5657(10)	16.9844(3)	9.4470(6)
α [°]	90	90	90
β [°]	93.6	101.177(2)	109.623(4)
γ [°]	90	90	90
V [Å^3]	1251.21(14)	3102.89(11)	3020.7(3)
Z	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.323 Mg	1.123	1.359
μ [mm^{-1}]	0.209	0.162	0.767
F(000)	528	1144	1304
crystal size [mm^3]	0.25×0.20×0.20	0.35×0.25×0.11	0.30×0.25×0.20
θ range for data collection [°]	1.99 to 30.51	2.60 to 30.03	2.26 to 30.51
index ranges	$-8 \le h \le 8$, $-18 \le k \le 18$, $-23 \le l \le 23$	$-18 \le h \le 18$, $-19 \le k \le 19$, $-23 \le l \le 23$	$-13 \le h \le 13$, $-51 \le k \le 51$, $-13 \le l \le 13$
reflections collected	19962	79976	58573
independent reflections	3818 [R(int) = 0.0509]	9069 [R(int) = 0.0462]	9122 [R(int) = 0.0395]
completeness to $\theta = 30.00°$ [%]	100.0	99.8	99.6
absorption correction	none	semiempirical from equivalents	semiempirical from equivalents
max. and min. transmission		1.000 and 0.983	0.8618 and 0.7192
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	3818/0/158	9069/0/337	9122/82/359
goodness-of-fit on F^2	1.023	1.027	1.040
final R indices [I > 2σ (I)]	$R1 = 0.0366$, w$R2 = 0.0912$	$R1 = 0.0359$, w$R2 = 0.0949$	$R1 = 0.0389$, w$R2 = 0.0838$
R indices (all data)			
$R1$	0.0600	0.0567	0.0560
w$R2$	0.1021	0.1000	0.0897
largest diff. peak and hole [e Å^{-3}]	0.451 and −0.182	0.809 and −0.297	1.004 and −0.641

gassed water, dried over Na_2SO_4, and filtered. Removal of solvent under vacuum left a yellow viscous oil. Crystallization from CH_2Cl_2/hexane gave single crystals (crystal data see Table 1). By concentration of the mother liquor a second fraction of white crystals, contaminated with small amounts of **4b** and **7b**, was obtained (total 118 mg). Yield of pure **6b** 79 mg (30%). Compound **6b**: ^{1}H NMR ([D$_8$]THF): δ=0.90 (s, 9H; CMe_3), 4.32 (br d, ^2J=14.1 Hz, 1H; NCH_2), 5.50 (br d, ^2J=14.1 Hz, 1H; NCH_2), 7.13 (tdd, ^3J=7.9, 7.0, $^4J_{P,H}$=1.6, ^4J=0.6 Hz, 1H; H-5), 7.40 (tt, ^3J=8.7, 6.9, ^4J+$^5J_{P,H}$=2.3 Hz, 1H; H-6), 7.83 (br d, ^3J=8.7 Hz, 1H; H-7), 8.03 (br dd, ^3J=7.9, $^3J_{P,H}$=4.3 Hz, 1H; H-4), 10.60 ppm (v br s, 1H; OH); ^{13}C{^{1}H} (DEPT) NMR ([D$_8$]THF): δ=28.69 (s; CMe_3), 35.96 (d, ^4J= 1.8 Hz; C_qMe_3), 55.37 (d, ^3J=3.8 Hz; NCH_2), 116.08 (s; CH-7), 121.03 (d, ^3J=13.0 Hz; CH-5), 126.91 (d, ^4J=3.4 Hz; CH-6), 130.07 (d, ^2J=21.9 Hz; CH-4), 142.46 (d, ^1J=37.0 Hz; C_q-3a), 147.29 (d, ^2J=7.7 Hz; C_q-7a), 162.65 (d, ^1J=53.0 Hz; C_q-2), 165.74 ppm (d, ^2J=21.8 Hz; C_q-COOH); ^{31}P{^{1}H} NMR ([D$_8$]THF): δ=118.71 ppm; MS (EI, 70 eV, 20°C): *m*/*z* (%): 250 (16) [*M*+1]$^+$, 249 (100) [*M*]$^+$, 193 (80), 161 (46), 148 (53); HRMS (ESI): *m*/*z*: calcd for $C_{13}H_{16}NO_2P$ [*M*+H$^+$]: 250.09916 (100); found: 250.09914.

1-(2,2-Dimethylpropyl)-2-trimethylsilyl-1*H*-1,3-benzazaphosphole (8b): KO*t*Bu (800 mg, 6.53 mmol) was added at −78°C to a solution of **1b** (174 mg, 0.85 mmol) in THF (5 mL) to give a yellow solution. *t*BuLi (0.52 mL, 0.89 mmol) was then added dropwise at the same temperature. This mixture was stirred for 4 h, while slowly warming to −10°C. The reaction mixture was again cooled to −78°C, and excess Me_3SiCl (1.07 mL, 8.48 mmol) was added dropwise, followed by stirring overnight at room temperature. THF was removed from the reaction mixture, and dry MeOH was added to quench unconverted *t*BuLi and Me_3SiCl. After the system had been kept for 4 h at room temperature, excess MeOH was removed under vacuum. The residue was extracted with diethyl ether, and the ether was removed in vacuum to give a yellow viscous oil (189 mg), which was identified by multinuclear NMR and HRMS as a mixture of **8b** and recovered **1b** (δ^{31}P=71.3 ppm) in 62:38 molar ratio based on ^{1}H NMR integration of CMe_3 protons (yield of **8b** 70% relative to converted **1b**). (Addition of *t*BuLi can be ruled out by NMR reaction monitoring of the crude reaction mixture). Compound **8b**. ^{1}H NMR ([D$_8$]THF): δ=0.46 (d, $^4J_{P,H}$=1.2 Hz, 9H; $SiMe_3$), 0.96 (s, 9H; CMe_3), 4.40 (br s, 2H; NCH_2), 7.05 (m, superimposed with **1b;** H-5), 7.27 (m, superimposed with **1b;** H-6), 7.79 (d, ^3J=8.6 Hz, 1H; H-7), 7.96 ppm (m, superimposed with **1b;** H-4); ^{13}C{^{1}H} (DEPT) NMR ([D$_8$]THF): δ=2.79 (d, $^3J_{P,H}$=9.1 Hz; $SiMe_3$), 29.65 (s; CMe_3), 35.97 (d, ^4J=1.6 Hz; CMe_3), 60.84 (d, ^3J=3.0 Hz; NCH_2), 116.06 (s; CH-7), 119.91 (d, ^3J=11.5 Hz; CH-5), 124.44 (d, ^4J=2.8 Hz; CH-6), 128.88 (d, ^2J=20.2 Hz; CH-4), 144.68 (d, ^1J=43.1 Hz; C_q-3a), 148.51 (d, ^2J=4.0 Hz, C_q-7a), 182.72 ppm (d, ^1J=75.0 Hz; C_q-2); ^{31}P{^{1}H} NMR ([D$_8$]THF): δ=126.67; MS (EI, 70 eV, 170°C): *m*/*z* (%)=277 (23) [*M*]$^+$, 220 (39), 73 (100) [$SiMe_3$]$^+$; HRMS (ESI in MeOH, NH_4OAc): *m*/*z*: calcd for $C_{15}H_{25}NPSi$: 278.14884 [*M*+H]$^+$; found: 278.14910. Experiments with smaller amounts of KO*t*Bu, from one to three equivalents relative to *t*BuLi, gave similar results.

Lithiation of 1c in diethyl ether: *t*BuLi (1.7 M pentane solution, 0.13 mL, 0.22 mmol) was added at −60°C to **1c** (50 mg, 0.19 mmol) in Et_2O (2 mL), the mixture was stirred at room temperature overnight, and the solvent was replaced with [D$_8$]THF. ^{31}P{^{1}H} NMR displayed a major peak at δ=−21.9 ppm (**4c**) and two small peaks at δ=−14.9 ppm (**3c**, uncertain) and δ=101 ppm (broadened, **2c**). The lack (or low intensity) of a PCH(Li)N resonance and the occurrence of a PCH_2N signal in the ^{13}C{^{1}H} (DEPT) NMR spectrum hint at the protonation of **3c** to **4c** within about 15 h (overnight). Compound **4c**: ^{13}C{^{1}H} (DEPT) NMR: δ= 26.70 (d, ^2J=14.3 Hz; PCMe_3), 30.81 (d, ^1J=20.4 Hz; PCMe_3), 31.01 (CH), 37.34 (CH_2), 39.91 (CH_2), 44.26 (small d, ^1J=18.4 Hz; PCH_2N), 56.21 (NC_q), 112.26 (CH-7), 116.05 (d, ^3J=8.5 Hz; CH-5), 126.23 (d, ^1J= 8.5 Hz; C_q-3a), 129.98 (CH-6), 133.37 (d, ^2J=24.0 Hz; CH-4), 153.55 ppm (s; C_q-7a).

1-Adamantan-1-yl-3-*tert*-butyl-2,3-dihydro-1*H*-1,3-benzazaphosphole-2-carboxylic acid (7c): *t*BuLi (1.5 M in pentane, 0.33 mL, 0.50 mmol) was added dropwise at −60°C to a solution of **1c** (123 mg, 0.46 mmol) in diethyl ether (2 mL). This mixture was allowed to warm slowly to room temperature and stirred for 5 h. The resulting orange-yellow solution was cooled to −60°C. Gaseous CO_2 (from dry ice) was introduced over a period of 90 min, leading to a color change from orange to yellow. A slight excess of Me_3SiCl (0.06 mL, 0.50 mmol) was added at the same temperature, and the mixture was stirred at room temperature overnight (colorless). Insoluble materials were filtered off and washed thoroughly with ether. Removal of the solvent gave a colorless semicrystalline slush. Treatment with dry MeOH (5 mL) and removal of volatiles in vacuum provided a solid that was recrystallized from CH_2Cl_2/hexane to give colorless microcrystals of **7c** (80 mg, 47%).M.p. 195–196°C; ^{1}H NMR (CD_2Cl_2): δ=0.98 (d, $^3J_{P,H}$=12.7 Hz, 9H; CMe_3), 1.73 (br s, 6H; δ-CH_2), 2.06 (br d, ^2J=11.9 Hz, 3H; β-CH_{2a}), 2.14 (br s, 3H; γ-CH), 2.32 (br d, ^2J=11.9 Hz, 3H; β-CH_{2b}), 4.75 (d, $^2J_{P,H}$=3.2 Hz, 1H; PCHN), 6.65 (tdd, ^3J=7.2, $^4J_{P,H}$=2.5, ^4J=0.7 Hz, 1H; H-5), 7.05 (br d, ^3J=8.4 Hz, 1H; H-7), 7.17 (tdd, ^3J=8.4, 7.2, ^4J=1.5 Hz, 1H; H-6), 7.28 ppm (td, ^3J= 7.2, $^3J_{P,H}$= 6.4, ^4J=1.5 Hz, 1H; H-4), OH/NH$^+$ below 12.5 ppm or v br; ^{13}C{^{1}H} (DEPT) NMR (CD_2Cl_2): δ=26.06 (d, ^2J=15.3 Hz; CH_3), 30.54 (s; CH), 31.75 (d, ^1J=23.4 Hz; CMe_3), 36.74 (s; CH_2), 40.21 (s; CH_2), 57.38 (br s; NC_q-1′), 59.86 (br d, ^1J=25.1 Hz; PCHN), 112.33 (s; CH-7), 116.52 (d, ^4J=9.1 Hz; CH-6), 122.77 (d, ^1J=9.1 Hz; C_q-3a), 130.11(s; CH-5), 132.75 (d, ^2J=24.3 Hz; CH-4), 152.48 (s; C_q-7a), 177.82 ppm (d, ^2J=16.5 Hz; CO); ^{31}P NMR (CD_2Cl_2): δ=7.37 ppm; HRMS: *m*/*z*: calcd for $C_{22}H_{30}NO_2P$ 371.2014; found: 371.2010.

3-*tert*-Butyl-1-(2,2-dimethylpropyl)-2,3-dihydro-1*H*-1,3-benzazaphosphole (4b) and 2-*tert*-butyl-1-(2,2-dimethylpropyl)-2,3-dihydro-1*H*-1,3-benzazaphosphole (10b): *t*BuLi (1.5 M in pentane, 0.31 mL, 0.47 mmol) was added dropwise at −30°C to **1b** (80 mg, 0.39 mmol) in pentane (2 mL). This mixture was allowed to warm slowly to room temperature and stirred for 20 h. Excess dry MeOH was added at room temperature to the reaction mixture, which was stirred overnight. Insoluble materials were filtered off and washed thoroughly with pentane. The solvent was removed under vacuum to give a colorless solid (100 mg, 97%) consisting of two components, **4b** and **10b** (75:25% by ^{1}H NMR integration of *t*Bu signals), which were characterized by NMR and HRMS (data for **10b** are in accordance with those below). Compound **4b**: ^{1}H NMR (C_6D_6): δ= 0.86 (s, 9H; CMe_3), 0.96 (d, $^3J_{P,H}$=12.0 Hz, 9H; $PCMe_3$), 2.38 (d, ^2J= 14.6 Hz, 1H; NCH_a), 2.91 (d, ^2J=14.6 Hz, 1H; NCH_b), 3.16 (dd, $^2J_{P,H}$= 2.3, ^2J=13.1 Hz; $PCH_{trans\ to\ t\text{-}Bu}N$), 3.59 (dd, ^2J=13.0, $^2J_{P,H}$=3.5 Hz, 1H; $PCH_{cis}N$), 6.44 (br d, ^3J=8.2 Hz; H-7), 6.72 (ddd, ^3J=7.3, $^4J_{P,H}$=2.3, ^4J= 0.8 Hz, 1H; H-5), 7.20 (dd, ^3J=8.5, ^4J=1.5 Hz, 1H; H-6), 7.45 ppm (ddd, ^3J=7.2, $^3J_{P,H}$=5.6, ^4J=1.4 Hz, 1H, H-4); ^{13}C{^{1}H} (DEPT) NMR (C_6D_6): δ=27.35 (d, ^2J=14.6 Hz; PCMe_3), 29.03 (s; CMe_3), 30.80 (d, ^1J=19.8 Hz; PCMe_3), 35.05 (s; CMe_3), 53.85 (d, ^1J=21.2 Hz; PCH_2N), 65.58 (s; NCH_2), 109.21 (s; CH-7), 117.87 (d, ^4J=7.8 Hz; CH-6), 124.60 (d, ^1J= 11.5 Hz; C_q-3a), 131.34 (s; CH-5), 132.89 (d, ^2J=21.9 Hz; CH-4), 157.96 ppm (s; C_q-7a); ^{31}P{^{1}H} NMR (C_6D_6): δ=−8.95 ppm; HRMS (ESI in MeOH, NH_4OAc): *m*/*z*: calcd for $C_{16}H_{27}NP$: 264.18756 [*M*+H]$^+$; found: 264.18765.

3-*tert*-Butyl-1-(2,2-dimethyl-propyl)-2,3-dihydro-1*H*-1,3-benzazaphosphole-2-carboxylic acid (7b) and *meso*-3,3′-bis[2-*tert*-butyl-1-(2,2-dimethyl-propyl)-2,3-dihydro-1*H*-1,3-benzazaphosphole] (10b): *t*BuLi (1.5 M in pentane, 0.50 mL, 0.75 mmol) was added dropwise at −30°C to a solution of **1b** (127 mg, 0.62 mmol) in pentane (2 mL). This mixture was allowed to warm slowly to room temperature and stirred overnight. The resulting orange-yellow solution was cooled to −60°C, and gaseous CO_2 (from dry ice) was introduced over a period of 90 min, leading to a color change from orange to yellow. A slight excess of Me_3SiCl (0.09 mL, 0.74 mmol) was then added at the same temperature, and the mixture was stirred at room temperature for 6 h (colorless). Insoluble material was filtered off and washed thoroughly with ether. Removal of the solvent gave a colorless semicrystalline substance, which was treated with dry MeOH (5 mL). Removal of volatiles in vacuum provided a viscous oil, which solidified on cooling and was recrystallized from saturated MeOH solution to give colorless **7b** (130 mg, 68%). Single crystals of **11b**, identified by X-ray crystal structure analysis as *meso*-**11b**, were grown by slow diffusion of aerial oxygen into the mother liquor containing the side product **10b**. ^{1}H NMR (CD_3OD): δ=1.01 (s, 9H; CMe_3), 1.03 (d, $^3J_{P,H}$=12.0 Hz, 9H; $PCMe_3$), 2.78 (dd, ^2J=15.3, $^4J_{P,H}$=2.0 Hz, 1H; NCH_A), 3.33 (dd, ^2J=15.9, $^4J_{P,H}\approx$2 Hz, 1H; NCH_B), 4.54 (d, $^2J_{P,H}$=2.7 Hz, 1H; $PCH_{cis}N$), 6.59 (br d,

^3J=8.4 Hz, 1H; H-7), 6.66 (tdd, ^3J=7.2, $^4J_{P,H}$=2.4, ^4J=0.6 Hz, 1H; H-5), 7.20 (td, ^3J=8.4, ≈7, ^4J=1.5 Hz, 1H; H-6), 7.24 (ddd, ^3J=7.2, $^3J_{P,H}$=6.0, ^4J=1.5 Hz, 1H; H-4), NH$^+$ with solvent OH at 4.96 ppm; ^{13}C{^{1}H} (DEPT) NMR (CD_3OD): δ=26.93 (d, ^2J=15.8 Hz; PCMe_3), 28.74 (s; CMe_3), 31.95 (d, ^1J=22.6 Hz; P*C*Me$_3$), 35.33 (s; *C*Me$_3$), 62.09 (s; NCH_2), 67.39 (d, ^1J=25.7 Hz; PCHN), 109.41 (s; CH-7), 117.88 (d, ^4J=8.1 Hz; CH-6), 122.25 (d, ^1J=11.8 Hz; C_q-3a), 131.57 (s; CH-5), 132.31 (d, ^2J=23.1 Hz; CH-4), 157.87 (s; C_q-7a), 176.77 ppm (d, ^2J=14.1 Hz; CO); ^{31}P NMR (CD_3OD): δ=19.50 ppm; MS (EI, 70 eV, 120 °C): m/z (%): 309 (2) $[M+1]^+$, 308 (9) $[M]^+$, 264 (11), 223 (16), 207 (57), 136 (40), 57 (100), 41 (72); HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{17}H_{26}NO_2P$ 307.17012; found: 307.1693.

3-*tert*-Butyl-1-(2,2-dimethylpropyl)-2-trimethylsilyl-2,3-dihydro-1*H*-1,3-benzazaphosphole ((*E*)-9b) and 2-*tert*-butyl-1-(2,2-dimethylpropyl)-2,3-dihydro-1*H*-1,3-benzazaphosphole ((*E*/*Z*)-10b): *t*BuLi (1.5 M in pentane, 0.14 mL, 0.21 mmol) was added dropwise at −30 °C to **1b** (35 mg, 0.17 mmol) in pentane (1 mL). This mixture was allowed to warm slowly to room temperature and stirred for 20 h. The reaction flask was again cooled to −60 °C, Me_3SiCl (0.03 mL, 0.236 mmol) was added dropwise, and the mixture was stirred at room temperature overnight. Insoluble material was filtered off and washed thoroughly with pentane. The solvent was removed under vacuum to give a colorless oil (50 mg) consisting of two components, (*E*)-**9b** and (*E*/*Z*)-**10b** (80:20 by ^{1}H NMR integration of *t*Bu signals), which were characterized by NMR and mass spectroscopic data. Compound (*E*)-**9b** exists as only one pair of diastereoisomers, while (*E*/*Z*)-**10b** forms a major and a minor pair of diastereoisomers, indicated by two ^{31}P signals and two sets of similar proton signals (partly superimposed).

Compound (*E*)-9b: ^{1}H NMR (C_6D_6): δ=0.12 (d, $^4J_{P,H}$=1.5 Hz, 9H; $SiMe_3$), 0.94 (s, 9H; CMe_3), 1.01 (d, $^3J_{P,H}$=12.1 Hz, 9H; $PCMe_3$), 3.05 (d, ^2J=14.9 Hz, 1H; NCH_a), 3.16 (d, ^2J=14.9 Hz, 1H; NCH_b), 3.76 (d, $^2J_{P,H}$=4.6 Hz, 1H; $PCH_{cis}N$), 6.36 (brd, ^3J=8.3 Hz, 1H; H-7), 6.64 (ddd, ^3J=7.2, $^4J_{P,H}$=2.5, ^4J=0.9 Hz, 1H; H-5), 7.16 (ddd, ^3J=8.3, 7.2, ^4J=1.5 Hz, 1H; H-6), 7.42 ppm (ddd, ^3J=7.2, $^3J_{P,H}$=5.7, ^4J=1.5 Hz, 1H; H-4); ^{13}C{^{1}H} (DEPT) NMR (C_6D_6): δ=0.68 (d, ^3J=9.3 Hz; 2-$SiMe_3$), 27.38 (d, ^2J=15.7 Hz; PCMe_3), 29.22 (s; CMe_3), 31.98 (d, ^1J=27.9 Hz; P*C*Me$_3$), 36.24 (s; *C*Me$_3$), 54.63 (d, ^1J=39.8 Hz; PCHN), 60.81 (s; NCH_2), 107.9 (s; CH-7), 116.68 (d, ^4J=8.0 Hz; CH-6), 123.09 (d, ^1J=10.7 Hz; C_q-3a), 131.36 (s; CH-5), 132.85 (d, ^2J=23.7 Hz; CH-4), 156.91 ppm (s; C_q-7a); ^{31}P{^{1}H} NMR (C_6D_6): δ=−1.70 ppm; HRMS: *m*/*z*: calcd for (*E*)-**9b** $C_{19}H_{34}NPSi$: 336.22709; found: 336.22712.

Compound (*E*/*Z*)-10b: ^{1}H NMR (C_6D_6): δ=0.81, 0.88 (2 s; CMe_3, 2-CMe_3), 2.97 (d, ^2J=15.2 Hz, 1H; NCH_A), 3.55 (d, ^2J=15.2 Hz, 1H; NCH_B), 3.72 (dd, ^3J=7.1, $^2J_{P,H}$=1.7 Hz, 1H; PCHN), 4.45 (ddt, $^1J_{P,H}$=183, ^3J=7.1, $^4J+J'$=2.3 Hz, 1H; P,H), 6.42 (brd, ^3J=8.3 Hz; H-7), 6.59 (ddd, ^3J=7.2, $^4J_{P,H}$=2.3, ^4J=0.9 Hz, 1H; H-5), 7.07 (tt, ^3J=8.3, 7.2, $^4J+J'$=2–3 Hz, 1H; H-4 or H-6); less intense diastereoisomer: 0.83, 0.89 (2 s; CMe_3, 2-CMe_3), 2.90 (d, ^2J=15.3 Hz, 1H; NCH_a), 3.45 (d, ^2J=15.3 Hz, 1H; NCH_b), 4.04 (brd, $^2J_{P,H}$=33 Hz, PCHN, uncertain), 4.42 (superimposed ddt, $^1J_{P,H}$=194, $J+J'$=4.5 Hz; PH, uncertain), 6.43 (d; H-7), 6.71 (tm; H-5), 6.60 ppm (tm; H-4 or H-6); H-6 or H-4 superimposed; ^{13}C{^{1}H} (DEPT) NMR (C_6D_6): δ=28.24 (d, ^3J=10.4 Hz; 2-CMe_3), 29.70 (s; CMe_3), 37.02 (s; *C*Me$_3$), 39.83 (d, ^2J=19.0 Hz; 2-*C*Me$_3$), 61.12 (s; NCH_2), 71.92 (d, ^1J=12.0 Hz; PCHN), 110.45 (s; CH-7), 117.79 (d, ^4J=9.0 Hz; CH-6), 120.15 (d, ^1J=4.6 Hz; C_q-3a), 130.56 (s; CH-5), 132.09 (d, ^2J=25.1 Hz; CH-4), 156.67 ppm (s; C_q-7a); minor diastereoisomer not detectable in ^{13}C NMR; ^{31}P{^{1}H} NMR (C_6D_6): δ=−82.28, −66.35 ppm, intensity ratio 80:20%.

Rhodium(η-P-3-*tert*-butyl-1-(2,2-dimethylpropyl)-2-trimethylsilyl-2,3-dihydro-1*H*-1,3-benzazaphosphole)(1,5-cyclooctadiene) chloride (12b): $[Rh(cod)Cl]_2$ (29 mg, 0.06 mmol) was added at −30 °C to the mixture of (*E*)-**9b** and (*E*/*Z*)-**10b** (40 mg, 0.12 mmol) dissolved in THF (1 mL), and the mixture was stirred at room temperature for 5 d. THF was partly removed, and the solution was overlayered with *n*-hexane to give colorless crystals of **12b**. A crystal taken from the mixture with the mother liquor was analyzed by X-ray diffraction and found to be a THF hemisolvate (crystal data see Table 1). The crystals were then separated, washed with hexane, dried (60 mg, 87%), and characterized by NMR. ^{1}H NMR (C_6D_6): δ=0.57 (s, 9H; $SiMe_3$), 0.89 (s, 9H; CMe_3), 1.48 (d, $^3J_{P,H}$=13.9 Hz, 9H; $PCMe_3$), 1.50–1.80 (brm, 4H; CH_2), 2.00–2.40 (brm, 4H; CH_2), 2.91 (d, ^2J=14.7 Hz, 1H; NCH_A), 3.15 (d, ^2J=14.7, $^4J_{P,H}$=1.8 Hz, 1H; NCH_B), 4.18 (m br, 1H; =CH), 4.49 (brm, 1H; =CH), 4.54 (d, $^2J_{P,H}$=10.8 Hz, 1H; PCHN), 5.42 (brm, 1H; =CH), 5.71 (brm, 1H; =CH), 6.36 (brd, ^3J=8.3 Hz, 1H; H-7), 6.53 (ddd, ^3J=7.2, $^4J_{P,H}$=2.7, ^4J=0.9 Hz, 1H; H-5), 7.10, 7.12 ppm (superimposed m, 2H; H-6, H-4); ^{13}C{^{1}H} (DEPT) NMR (C_6D_6): δ=5.52 (d, ^3J=3.9 Hz; 2-$SiMe_3$), 28.35 (d, J=2.0 Hz; CH_2), 29.05 (s; CMe_3), 30.87 (d, ^2J=6.4 Hz; PCMe_3), 30.20 (brs; CH_2), 33.31 (brs; CH_2), 34.62 (d, J=3.9 Hz; CH_2), 35.74 (s; *C*Me$_3$), 38.77 (d, ^1J=6.6 Hz; P*C*Me$_3$), 57.70 (d, ^1J=5.1 Hz; PCH), 63.31 (d, ^3J=4.1 Hz; NCH_2), 65.29 (d, $J_{Rh,C}$=13.6 Hz; CH=), 70.84 (d, $J_{Rh,C}$=13.4 Hz; CH=), 101.39 (dd, $J_{Rh,C}$=7.8, J=14.5 Hz; CH=), 104.04 (dd, $J_{Rh,C}$=7.8, J=11.3 Hz; CH=), 109.46 (d, ^3J=4.0 Hz; CH-7), 117.47 (d, ^3J=9.2 Hz, CH-5), 118.13 (dd, ^1J=28.4 Hz; C_q-3a), 131.57 (d, ^2J=9.2 Hz; CH-4), 132.59 (brs; CH-6), 157.29 ppm (s; C_q-7a); ^{31}P{^{1}H} NMR (C_6D_6): δ=33.54 ppm (d, $^1J_{Rh,P}$=150.7 Hz); HRMS (ESI): calcd for $C_{27}H_{46}ClNPRhSi$: 546.21872 $[M-Cl]^+$; found: 546.21867 (strong tendency to formation of Rh clusters observed in ESI HRMS measurements).

Compound 4b as a ligand in palladium-catalyzed C–N coupling of 2-bromopyridine with mesitylamine: Toluene (5 mL) was placed in an oven-dried Schlenk vessel charged with 2-bromopyridine, 2,4,6-trimethylaniline, palladium acetate or $Pd_2(dba)_3$, **4b**, and NaO*t*Bu (amounts see Table 2). The resulting deep red-brown mixture was heated for 48 h at 100 °C and was then allowed to cool to room temperature, and diethyl ether (5 mL) was added. The resulting mixture was washed with brine, and the organic layer was dried over Na_2SO_4 and concentrated in vacuum. The remaining yellow oily product was purified by column chromatography on silica gel with ethyl acetate/hexane (10%) as eluent to give pure 2-mesitylaminopyridine as a colorless solid. NMR data are in accordance with reported values.[19]

Table 2. Pd-catalyzed coupling of 2-bromopyridine with 2,4,6-trimethylaniline.

2-Bromopyridine [g (mmol)]	Mes-NH_2 [g (mmol)]	Pd source [mg (mol%)]	Ligand [mg (mol%)]	NaO*t*Bu [mg (mmol)]	Yield [mg (%)]
0.32 (2.0)	0.325 (2.4)	$Pd(OAc)_2$ 2.2 (0.5)	5 (1.0)	27 (2.8)	180 (13)
0.16 (1.0)	0.162 (1.2)	$Pd(OAc)_2$ 11 (5.0)	13 (5.0)	134 (1.4)	65 (29)
0.16 (1.0)	0.162 (1.2)	$[Pd_2(dba)_3]$ 46 (5.0)	20 (7.5)	134 (1.4)	120 (53)

Compound 7b as a ligand in nickel-catalyzed ethylene oligomerization: Compound **7b** (20.0 mg, 65 μmol) and $Ni(COD)_2$ (17.9 mg, 65 μmol) were dissolved in toluene (each in 10 mL) and mixed at room temperature. The resulting orange-yellow solution was stirred at room temperature for 30 min and transferred into an argon-filled stainless steel autoclave (75 mL). The autoclave was pressurized (ca. 50 bar) with ethylene (12.3 g) and put in a silicon oil bath. After heating for ca. 15 h at 70 °C, cooling to room temperature, and weight measurement, unconverted ethylene (together with some butenes) was released through a cooling trap (−70 °C, no liquid condensate). The polymer with solvent and oligomers was then transferred to a flask, and all volatiles were flash-distilled at 3–4 mbar/70–80 °C into a cooling trap (−196 °C) and analyzed by GC (total of oligomers 0.6 g, of which 0.07 g butenes, 0.13 g hex-1-ene, 0.14 g oct-1-ene, 0.08 g dec-1-ene, small amounts of other olefins). The residual polymer was extracted with a mixture of methanol and concentrated hydrochloric acid (each 25 mL) by stirring overnight at room temperature, and was then washed with methanol and dried in vacuum, yielding waxy PE (11.0 g), m.p. 115–117 °C, ρ 0.91 g cm^{-3}. ^{1}H NMR (in C_6D_5Br at 100–110 °C after swelling for 1 d at 120 °C; more details see earlier report[21a]) integration ratios of vinyl, alkene, CH_2, and CH_3 indicate 78/22% α-olefins, 1.6 Me/Vin, 30 Me/1000 C, M_{NMR} 725 g mol^{-1}. The conversion was=

11.6 g (=94%, oligomers in MeOH/HCl extract not determined), TON= 6360.

Crystal structure analyses: Crystals of **6b, 11b,** and **12b** were mounted on glass fibers in inert oil. Data were recorded at low temperature on a Bruker SMART 1000 CCD (**6b**, **12b**) or an Oxford Diffraction Xcalibur S diffractometer (**11b**) using MoK_α radiation ($\lambda = 0.71073$ Å). Crystal data are summarized in Table 1. The structures were solved by direct methods and refined by full-matrix, least-squares on F^2.[22] Hydrogen atoms were included by use of a riding model or rigid methyl groups (exceptions: OH refined freely for **6b**, H of coordinated double bonds refined freely for **12b**). The THF in **12b** is disordered over an inversion centre.

CCDC 657442 (**6b**), 671405 (**11b**), and 657443 (**12b**) 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.

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