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Enantiomerically Pure N Chirally Substituted 1,3-Benzazaphospholes: Synthesis, Reactivity toward *t*BuLi, and Conversion to Functionalized Benzazaphospholes and Catalytically Useful Dihydrobenzazaphospholes

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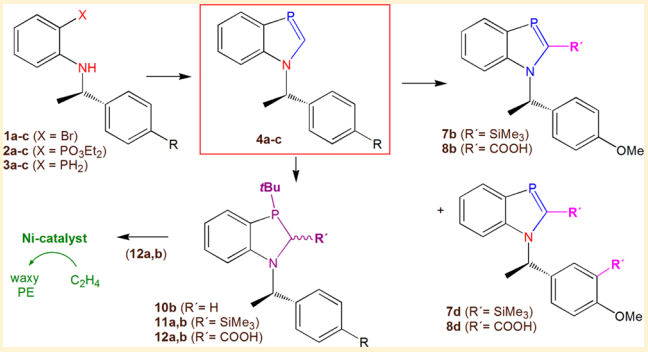
Supporting Information

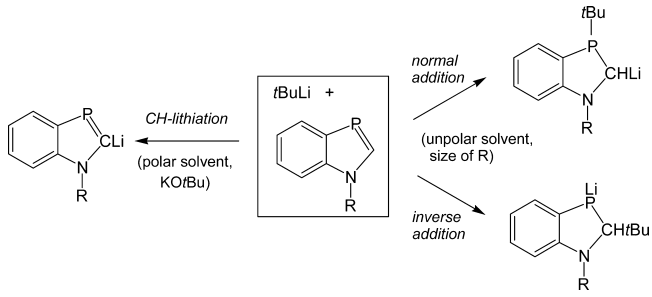
ABSTRACT: Catalytic C−P coupling of chiral *o*-bromoanilines **1a−c** to the corresponding *o*-phosphonoanilines **2a−c**, reduction to the phosphines **3a−c**, and final acid-catalyzed cyclocondensation represents a convenient access to the title compounds **4a−c**. Reaction of **4a,b** with *t*BuLi allows solvent-dependent directed lithiation leading either to 2-lithiobenzazaphospholes with a −P═CLi−NR− substructure (in Et_2O/KO*t*Bu), in the case of anisyl substitution accompanied by partial additional lithiation in *o*-position of the MeO-group, or to regiospecific "normal" addition with formation of −P(*t*Bu)−CHLi−NR− species. These were trapped by $ClSiMe_3$, CO_2, or MeOH to give the corresponding substitution products **7b**, **8b**, **10b**, **11a,b** and **12a,b**, respectively. **12a,b**, containing the P−C−COOH structural unit, forms with $Ni(COD)_2$ in THF very efficient ethylene oligomerization catalysts with high selectivity for linear α-olefins. The structure elucidation of the products is based on conclusive solution NMR data and crystal structure analyses of the 1-(1*S*)-anisylethyl compounds **3b** and **4b**.



INTRODUCTION

1,3-Benzazaphospholes[1,2] constitute a special type of trivalent phosphorus compound. Like the more familiar phosphabenzenes (phosphinines),[3] they exhibit dicoordinated phosphorus and aromatic stabilization,[4] but the presence of the nitrogen electron lone-pair in a position β to phosphorus, supported by the inductive electron-withdrawing effect of nitrogen, induces increased π density in the ring and at phosphorus and changes the reactivity. Whereas the stability of complexes with transition-metal ions is lowered, and tilted or even side-on P coordination with π-donor contributions is favored for d^{10} cations[5] over coordination within the ring plane, preferred in phosphinine complexes,[3] the α-metalated 2-lithiobenzazaphospholes[6] are more stable than 2-lithiophosphinines.[7] This allows CH lithiation of the -P═CH−NR− structural unit in competition with the usual addition of *t*BuLi at the P═C double bond and reaction control by solvent and auxiliaries (Scheme 1). The -P═CLi−NR− species open organometallic routes to new σ^2P hybrid ligands,[6] and the highly reactive −P(*t*Bu)−CHLi−NR− addition products offer novel strategies to synthesize bulky P-*tert*-butyl- and 2-substituted heterocyclic dialkyl(*o*-amino)aryl-type phosphine ligands.[6a,8] The nature and size of the N substituents play an important role in the reaction control. The small methyl group favors CH lithiation in polar solvents and "inverse" addition in toluene, whereas reactions in hexane provide a mixture of "normal" and "inverse" addition products. Bulky N-alkyl groups, however, disfavor CH lithiation in polar solvents and "inverse" addition in hexane and enable clean "normal" addition in the latter solvent. This behavior raises the question whether an asymmetric substituent at nitrogen might also induce stereoselectivity in the "normal" addition at the P═C bond and prompted us to explore a

Scheme 1. Reaction Modes of N-Substituted 1,3-Benzazaphospholes with *t*BuLi



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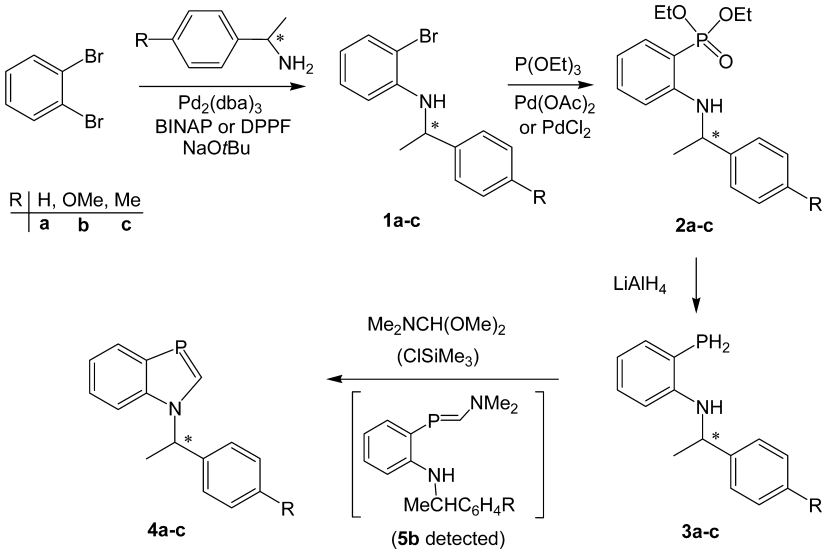
Scheme 2. Synthesis of 1−4



convenient route to such benzazaphospholes and to test their reactivity.

RESULTS AND DISCUSSION

Synthesis. Commercially available chiral (1*S*)-1-arylethylamines were chosen as starting materials to promote stereoselection in the addition reactions of the title compounds with *t*BuLi by different sizes and shapes of the α substituents. The substituent in the para position of the phenyl group was varied, partially to simplify the NMR spectra and partially to see if this affects the reactivity toward *t*BuLi. The primary arylethylamines were coupled with *o*-dibromobenzene using the Buchwald−Hartwig protocol[9] with various Pd−phosphine catalysts and NaO*t*Bu as a base. The moderate steric hindrance at the amino group by the α-branched substituent favored the arylamination and allowed high yields of **1a−c** (Scheme 2) with a catalyst formed from $Pd_2(dba)_3$ and BINAP (Table 1, entries 1−3) and good yields with a $Pd_2(dba)_3$/DPPF catalyst (entries 4−6), whereas monodentate phosphine ligands and $Pd(OAc)_2$ or $Pd(PPh_3)_4$ were much less suitable (entries 7 and 8). In the absence of catalyst under otherwise identical conditions, no conversion was observed. The products were isolated as pale yellow viscous oils after column chromatography on silica. In the second step, phosphorus was introduced. As found in our earlier studies,[2c] the C−P coupling of bulkily substituted N-secondary *o*-bromoanilines can be achieved in high yields with excess triethyl phosphite in the presence of $Pd(OAc)_2$ or $PdCl_2$ under the conditions of the Tavs reaction.[10] The milder conditions of the Hirao coupling with diethyl phosphite in the presence of a base[11] had no advantages in these particular couplings and required time-consuming optimization and additional auxiliary phosphine ligands. Therefore, we tested the Tavs coupling of **1a−c** with triethyl phosphite in the presence of $NiCl_2$, $NiBr_2$, $PdCl_2$, and $Pd(OAc)_2$, respectively. The Ni(0) complexes, formed on heating with $P(OEt)_3$ at 180−200 °C (detected by NMR in the absence of **1**), did not catalyze the P−C coupling, but the Pd(0) triethyl phosphite complexes, generated under similar conditions from excess $P(OEt)_3$ and $PdCl_2$ (6 mol %) or $Pd(OAc)_2$ (3 mol %), proved amine-tolerant and afforded the N-secondary *o*-phosphonoanilines **2a−c** in high yields: 80−84% after purification by column chromatography on silica. These were reduced by $LiAlH_4$ in good yields (ca. 70%) to the corresponding 2-phosphinoanilines **3a−c**, air-sensitive oils (**3a**) or solids (**3b,c**) of unpleasant odor, and finally cyclized with dimethylformamide dimethylacetal (DMFA) to the 1,3-benzazaphospholes **4a−c**. In the absence of catalyst the cyclization required heating for 5 days at 50 °C. After 2 days, NMR monitoring of the conversion of **3b** displayed signals of **4b** ($\delta(^{31}P)$ 73.2 ppm), phosphaalkene **5b** (R* = (*S*)-CH(*p*-anisyl)Me, $\delta(^{31}P)$ 43.9 ppm, isomer ratio *E*:*Z* 9:1), and its symmetric cyclodimer, a 1,3-diphosphetane ($\delta(^{31}P)$ −27.0 ppm), with an intensity ratio of 55:20:25. After 7 days at 50 °C **4b** was isolated in 81% yield. In the presence of chlorotrimethylsilane the reaction is much faster and complete within 1 day. This reagent, used in stoichiometric amounts, silylates any of the nucleophilic sites and thereby liberates HCl as the catalyst of the cyclocondensation. After extraction of N-basic impurities with dilute aqueous sulfuric acid the title compounds were isolated as moderately air-sensitive, nearly colorless viscous oils (**4a,c**) or a pale yellow solid (**4b**), crystallizing by slow diffusion of hexane into the concentrated THF solution.

Table 1. Pd-Catalyzed Coupling of 1,2-Dibromobenzene with (1*S*)-1-Phenylethylamines

entry	ligand (amt, mol %)	Pd compd (amt, mol %)	base (amt, equiv)	product (yield, %[a])
1	BINAP (7.5)	$Pd_2(dba)_3$ (5)	NaO*t*Bu (1.4)	**1a** (74)
2	BINAP (7.5)	$Pd_2(dba)_3$ (5)	NaO*t*Bu (1.4)	**1b** (75)
3	BINAP (7.5)	$Pd_2(dba)_3$ (5)	NaO*t*Bu (1.4)	**1c** (74)
4	DPPF (7.5)	$Pd_2(dba)_3$ (5)	NaO*t*Bu (1.4	**1a** (57)
5	DPPF (7.5)	$Pd_2(dba)_3$ (5)	NaO*t*Bu (1.4)	**1b** (59)
6	DPPF (7.5)	$Pd_2(dba)_3$ (5)	NaO*t*Bu (1.4)	**1c** (58)
7	$P(o\text{-Tol})_3$ (5)	$Pd(OAc)_2$ (3.0)	NaO*t*Bu (1.4)	**1b** (6)
8		$Pd(PPh_3)_4$	Et_3N	**1b** (0)

[a]Yield after isolation.

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Structural Aspects. All of the new compounds were characterized by conclusive ^{1}H, ^{13}C, and also (except for **1a−c**) ^{31}P solution NMR data, by $[M + H]^+$ peaks in the ESI-HRMS spectra, and (for solids) by satisfactory elemental analysis. Typical chemical shift ranges and coupling constants with the ^{31}P nuclei allowed unambiguous assignment of the signals and clear identification of the compounds. The phosphorus resonances of the intermediate phosphaalkenes **5b** appear at somewhat higher field than the signals of **4a−c**, and the $^{2}J_{PH}$ coupling constant of the major *trans* isomer of **5b** is significantly smaller (13.9 Hz) than in **4a−c** and in the trace of *cis*-**5b** (37.8 Hz), as is typical for Me_2N- and Me_3SiO-substituted *trans*-phosphaalkenes.[12]

Additional and more detailed structure information was obtained by X-ray diffraction of single crystals of **3b** and **4b**, both crystallizing from THF/hexane in the monoclinic chiral space group $P2_1$ with two molecules in the unit cell. The absolute configuration was determined by anomalous dispersion, confirming the *S* configuration at the α-C atom of the N substituents. Bond lengths and angles are within the usual ranges. For *o*-phosphinoaniline **3b** (Figure 1) all hydrogen

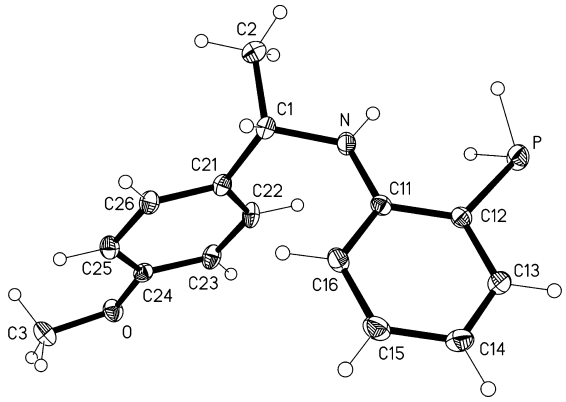

Figure 1. Molecular structure of **3b** in the crystal (ellipsoids with 50% probability). Selected bond lengths (Å) and angles (deg): P−C12 1.8215(9), O−C24 1.3716(10), O−C3 1.4253(12), C1−C21 1.5205(11), C1−C2 1.5275(12), C11−C16 1.4069(12), C11−C12 1.4189(12), C12−C13 1.3978(12); C11−N−C1 124.18(7), C24−O−C3 117.73(7), N−C1−C21 113.04(7), N−C1−C2 108.43(7), C21−C1−C2 109.61(7), N−C11−C16 121.24(7), N−C11−C12 120.05(7), C13−C12−P 116.77(6), C11−C12−P 124.35(6).

atoms at P and N were found and refined freely. The phosphino group adopts an intersecting conformation with dihedral angles of 47.6(8) and −47.6(7)°, respectively, for C11−C12−P−H02 and C11−C12−P−H03. The phosphorus lone pair then lies in the ring plane, indicating a lack of π interactions, as was similarly shown for gaseous *o*-phosphinophenol and the analogous arsine by combined photoelectron spectroscopic and quantum chemical studies.[13] For the amino group the situation is different. The small dihedral angle of 2.28(12)° for C1−N−C11−C16 and short N−C11(sp^2) and N−C1(sp^3) bond lengths (1.3746(10) and 1.4581(10) Å) indicate sp^2 hybridization of nitrogen and efficient π conjugation. The packing (for Figure S1 see the Supporting Information) displays only weak intermolecular P−H···π and *o*-C−H···π contacts to the π-rich amino- and methoxy-substituted phenyl groups of neighboring molecules, but no π stacking. The intramolecular (N)H01···P contact (2.732(14) Å) is only slightly shorter than the sum of the van der Waals radii (3.0 Å[14]). The orientation of the phosphine hydrogen atoms toward the amine proton might imply weak N−$H^{\delta+}$···$^{\delta-}$H−P interactions, but the H01···H(P) distances (2.27, 2.35 Å) are only marginally shorter than the sum of the van der Waals radii (2.4 Å,[14] which may of course depend on the chemical environment). Interactions with the P lone pair would require the opposite orientation of the PH_2 group.

The chiral benzazaphosphole **4b** (Figure 2) displays the expected planarity of the fused ring system (mean deviation

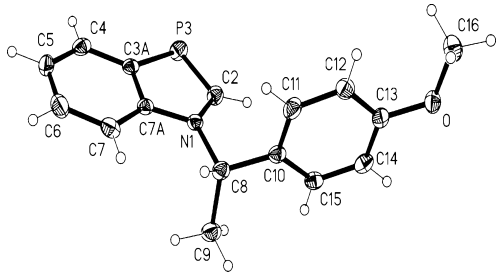

Figure 2. Molecular structure of **4b** in the crystal (ellipsoids with 50% probability). Selected bond lengths (Å) and angles (deg): P3−C2 1.7189(14), P3−C3A 1.7842(12), N1−C2 1.3578(16), N1−C7A 1.3855(16), N1−C8 1.4922(17), C8−C9 1.5177(18), C8−C10 1.5188(17); N1−C2−P3 115.56(10), C2−P3−C3A 88.28(7), C2−N1−C7A 112.55(11), C2−N1−C8 124.42(11), C7A−N1-C8 122.72(10), C4−C3A-P3 130.11(11), C7A-C3A-P3 111.34(10), N1−C8−C9 109.57(10), N1−C8−C10 110.73(11), C9−C8−C10 115.34(12), C13−O−C16 116.89(11).

0.005 Å) with C8 lying 0.12 Å out of the plane. The N−C2 and P−C2 bonds are short in comparison to the N−C7A and P−C3A bonds, as is typical for 1,3-benzazaphospholes.[1] With respect to 1-neopentyl-1,3-benzazaphosphole,[2c] bearing a moderately bulky primary N-alkyl group, the P−C2 (double) bond is perhaps marginally longer (by 0.0087(14) Å), but N−C2 and the other bonds of the ring system are very similar. The α-methyl group at C8 is rotated into a position almost perpendicular to the benzazaphosphole ring plane (C2−N1−C8−C9 88.08(14)°), whereas the phenyl group is in a *gauche* position on the same side as C2 (C2−N1−C8−C10 40.26(16)°), and its ring plane is nearly perpendicular to that of the benzazaphosphole-C8 plane (N1−C8−C10−C11 77.21(15)°). π interactions with lithium, shown for various lithium arene compounds,[15] should direct *t*BuLi with the organic residue toward 2-CH and might activate *t*BuLi species for stereoselective addition at the P═C2 bond. Additionally, interactions with the O-donor group may have an impact on the reactivity.

Reactivity of 4a−c. General aspects of the reactivity of 1,3-benzazaphospholes, shown earlier, are the aromaticity, proved by photoelectron spectroscopic and quantum chemical studies,[4b] and the resulting stabilization of the −P═CR′−NR− species toward attack by water, aqueous acids, and bases and several other electrophilic and nucleophilic reagents.[1,2,6] This includes even organolithium reagents in polar solvents such as diethyl ether and THF and renders feasible the CH lithiation of 1-methylbenzazaphospholes with R′ = H to give isolable −P═CLi−NMe− reagents, stable at room temperature up to 2 days.[6b,c] Bulky N substituents, however, favor competing addition reactions,[6a] and the use of nonpolar solvents causes complete suppression of the CH lithiation, even for 1-methyl-1,3-benzazaphospholes.[8]

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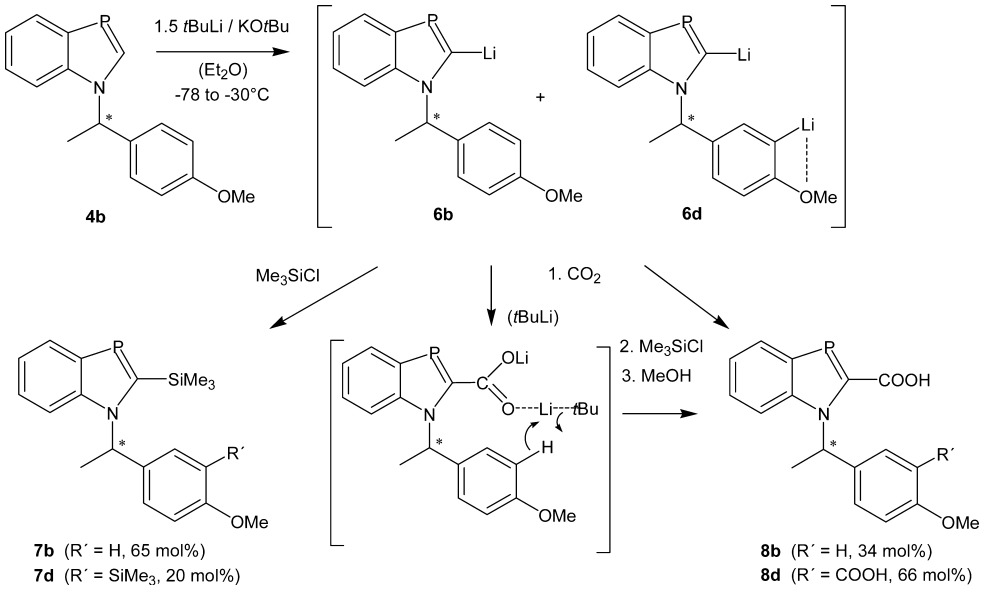
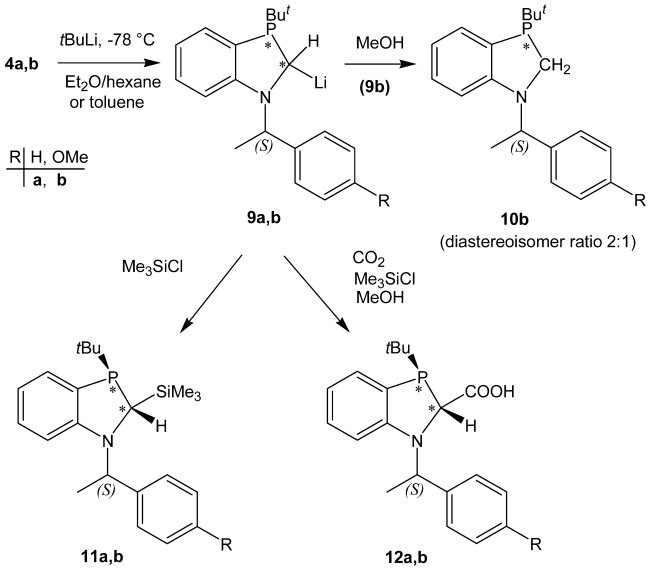
Scheme 3. Lithiation of 4b in the Presence of KO*t*Bu in Ether and Conversion to Silylated and Carboxylated Products



The focus of the reactivity study of the N asymmetrically substituted compounds **4** is the addition of *t*BuLi and possible stereocontrol, but the question of maintenance of preferred 2-CH lithiation in polar solvents or the dominance of directed lithiation in *o*-position of the methoxy group[16] of the *p*-anisyl-substituted **4b** was also addressed and is presented first. In these experiments lithiation was carried out by addition of the *t*BuLi pentane solution to an ethereal solution of **4b** and KO*t*Bu at −70 °C and subsequent slow warming to −30 °C. Under these mild conditions ether cleavage is avoided, but the reaction is slow despite the fact that the alkoxide supports the CH lithiation to **6** via highly polar *t*BuLi/KO*t*Bu clusters.[17] An excess of *t*BuLi (1.5 equiv) was required to achieve nearly quantitative conversion of **4b**. The lithiated species were trapped by $ClSiMe_3$ and in a second experiment by CO_2. Workup, in the latter case via silylation of the lithium carboxylate and methanolysis of the silyl ester after separation of LiCl, provided the *N*-anisylethyl-substituted 2-(trimethylsilyl)- and 2-carboxybenzazaphospholes **7b** and **8b** accompanied by **7d** and **8d** with additional $SiMe_3$ and COOH groups in a position ortho to the methoxy group (Scheme 3). The molar ratio **7b**:**7d** was ca. 3:1 and that of **8b**:**8d** 1:2, on the basis of integration of methyl proton signals. The detection of a minor amount of **4b** in the first reaction and the dominance of **8d** in the second reaction, both without hints of solely lithiation in *o*-position of the OMe group, suggests that the methoxy-directed lithiation is favored after the first lithiation step to **6b** and competes then with CH lithiation of **4b**. This does not allow a selective monolithiation of **4b** under the above conditions. The higher amount of ortho lithiation product **8d** in the reaction with CO_2 in comparison with that in the trimethylsilylation (**7d**) can be explained by incomplete consumption of *t*BuLi before addition of the trapping reagents and carboxylate-supported additional ortho lithiation. The high content of **7b** is in accordance with continued 2-CH lithiation by unconverted *t*BuLi in the presence of $ClSiMe_3$, since trapping of the bulky *t*BuLi by $ClSiMe_3$ occurs only at higher temperature.

When the lithiation was carried out in the absence of KO*t*Bu in THF (−70 to −30 °C) the CH lithiation to **6d** was still preferred but was accompanied by considerable amounts of the addition product **9b**. The latter is highly reactive and rapidly deprotonates THF, so that trapping with $ClSiMe_3$ afforded a mixture of **7b** with **10b**. Dominant or exclusive addition was achieved in less polar solvent systems. Methanolic quenching of the lithiation products formed in a 1:1 mixture of hexane and diethyl ether gave evidence that the addition is strongly preferred to CH lithiation, is regiospecific for the "normal" addition, and is moderately diastereoselective with respect to the asymmetric (1*S*)-carbon at nitrogen (Scheme 4). NMR

Scheme 4. Addition of *t*BuLi at 4a,b Followed by Protonation, Silylation, or Carboxylation



inspection of the crude product mixture displayed only 13 mol % of **4b** as the quenching product of **6b** and a 2:1 preference of one of the diastereosiomers of **10b** to the other (58 vs 29 mol %). When only hexane or toluene was used as solvent, CH lithiation was completely suppressed in favor of regiospecific "normal" addition but the diastereoselectivity was lower or entirely lost. Thus, in hexane two diastereoisomers of the

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silylation trapping product **11b** were formed in a 1:1 ratio, whereas reaction in hexane/Et_2O (1:1) furnished these diastereoisomers in a ratio of 62:38. The analogous reaction of **4a** provided the diastereoisomers of **11a** similarly in a 65:35 ratio. Lack of signals for two further diastereoisomers involving the new chirality center at C2 indicates high diastereoselectivity for the trimethylsilylation, yielding only the products with *t*Bu and $SiMe_3$ groups at *trans* positions. This assignment is evident from the rather small $^2J_{PH}$ coupling constants of the PCH protons (4.2−4.9 Hz) which hint at an orientation of this proton *trans* to the P lone-pair (*syn* toward *t*Bu) and thus also of the substituents at the adjacent C and P atoms. Trapping with CO_2, followed by silylation and methanolysis of the silyl ester after separation from LiCl, likewise gave two major diastereoisomers of **12a** and **12b**, respectively, both with small $^2J_{PH}$ values (2.3−2.6 Hz) and thus *trans* positions of *t*Bu and COOH, but the selectivity of the substitution was lower and led also to minor and/or trace amounts of the two other possible diastereoisomers. It should be noted here that the 2,3-dihydro-1,3-benzazaphospholes are kinetically less stable than the aromatic benzazaphospholes. Slow chromatography on silica gel led to major decomposition of the dihydrobenzaphosphole-2-carboxylic acid, while storage in solution or flash chromatography may cause acid-catalyzed isomerization, as observed also for 1,3-azaphospholidine-2-carboxylic acids.[18] This proceeds probably via slow ring-opening/ring-closure reactions at the aminophosphinoacetalic structure unit. For **12b** such isomerization was observed after a small amount of pivalinic acid was separated by flash chromatography on silica gel using hexane/ethyl acetate (2%) for elution. The NMR spectra then displayed a change of the diastereoisomer composition. A phosphorus resonance at 8.5 ppm, observed for a minor isomer of **12a** but not for crude **12b**, became the second strongest signal while the previously second most intense signal at 17.9 ppm became much smaller. In the proton and ^{13}C NMR spectra a new PCH doublet appeared for this isomer, shifted slightly downfield with an increased $^2J_{PH}$ (7.6 Hz) and slightly increased $^1J_{PC}$ (ΔJ = 1.3 Hz) coupling constant, whereas the $^2J_{PC}$ coupling constant of the COOH carbon resonance, 15.9 Hz in both of the diastereoisomers A and B, becomes 0. This hints at the formation of a new diastereoisomer with *trans* positions (*gauche conformations*) of 2-H and the P lone pair and of *t*Bu and COOH, possibly favored by hydrogen bond interactions of the COOH with the amino group. An unusually fine splitting of the multiplet of the two ortho protons with an otherwise typical AA′BB′ coupling pattern hints at weak through-space interactions to the P lone pair in diastereoisomer C (Figure 3). Since the N substituent has an *S* configuration and the *o*-H···P interaction requires an orientation of the anisyl group more or less perpendicular to the NC_6H_4P plane with the P lone pair directed toward the anisyl group, the P atom in diastereoisomer C also has an *S* and C2 an *R* configuration. Single crystals for more direct information on the configuration at phosphorus and C2 also in the primarily formed diastereoisomers A and B have not been obtained so far.

Examples of Complexes and Use in Catalysis. The ligand properties of 1,3-benzazaphospholes and dihydrobenzazaphospholes differ sharply. The former are weak donors, form labile complexes with d^{10} cations,[5] and need π back-bonding for stable complexes, e.g. $LM(CO)_5$ (M = Cr, Mo, W), indicated by a low downfield (Cr) or even upfield (Mo, W) ^{31}P coordination chemical shift.[1,2] The *P-tert*-butyl-2,3-dihydro-1,3-benzazaphospholes, however, are P-basic phosphines which

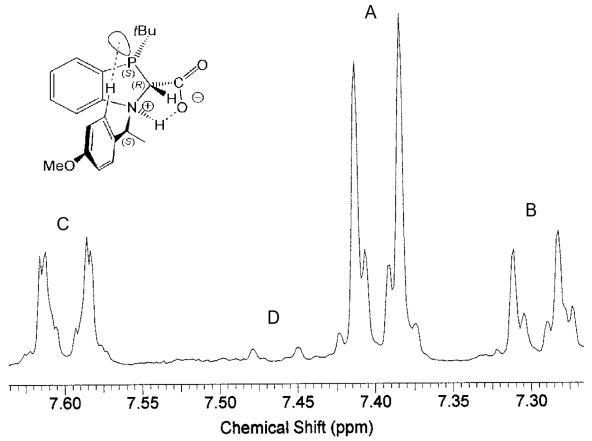

Figure 3. *o*,*o*′-Proton multiplets of **12b** with fine splitting for diastereoisomer C (right end of B multiplet partially superimposed by 4-H).

display downfield coordination chemical shifts.[19] For the 1-(1*S*)-arylethyl-benzazaphospholes and dihydrobenzazaphospholes these properties are each demonstrated by one example: the tungsten(0) pentacarbonyl complex **13b** and the Rh(COD)Cl complex **14b** (Chart 1). The former displays the typical upfield coordination chemical shift in comparison to the ligand **4b** ($\Delta\delta(^{31}P)$ = −39.4 ppm), whereas the latter exhibits the expected downfield shifts of the diastereoisomers versus **11b** ($\Delta\delta(^{31}P)$ ≈ 40 ppm). Attempts to separate the diastereoisomers of **11b** failed. The structures of the complexes were elucidated by conclusive ^{13}C and proton NMR data with characteristic changes of the $^1J_{PC}$ coupling constants by the complexation.

The dihydrobenzazaphosphole-2-carboxylic acids **12** imply a P−C−COOH structural unit, as in diphenylphosphinoacetic acid, originally used for the generation of nickel catalysts for the oligomerization of ethylene in the Shell Higher Olefin Process.[20] Therefore, they might also be suitable for generation of PO^- chelate catalysts.[21] The bulky *tert*-butyl group and increased π density at the aryl carbon in a position ortho to the amino group, along with steric shielding of the N-donor site by the branched arylethyl substituent, should even improve the efficiency of the nickel catalysts for the oligomerization of ethylene, and this prompted us to screen **12a**,**b** for this purpose in a batch procedure. The precatalysts were prepared in situ from equimolar amounts of the ligands and Ni(1,5-COD)$_2$ in THF, transferred into a stainless steel autoclave, and after pressurization heated to 70 °C. As in a preliminary test of 1-neopentyldihydrobenzazaphosphole-2-carboxylic acid,[6a] the nickel complexes generated with Ni(COD)$_2$ formed very active catalysts during heating and, after reaching about 70 °C, converted ethylene rapidly, as seen by the pressure−time curve, depicted in Figure 4. The catalyst formation and conversion were slightly slower for **12a**,**b**/Ni than for the analogous 1-neopentyl-substituted catalyst, but the conversion was almost quantitative. The turnover numbers were limited by the catalyst/ethylene ratio. Waxy polymers and a small portion of liquid oligomers were provided (Table 2). NMR analysis of the waxy oligomers showed high selectivity for linear α-olefins (87−89%) and molecular weights (M_{NMR}) between 750 and 900, on the basis of the integral ratios of olefinic to CH_2 and CH_3 protons of swollen polymers (measured at 100 °C). The oligomers, analyzed by GC of the flash distillate, were also

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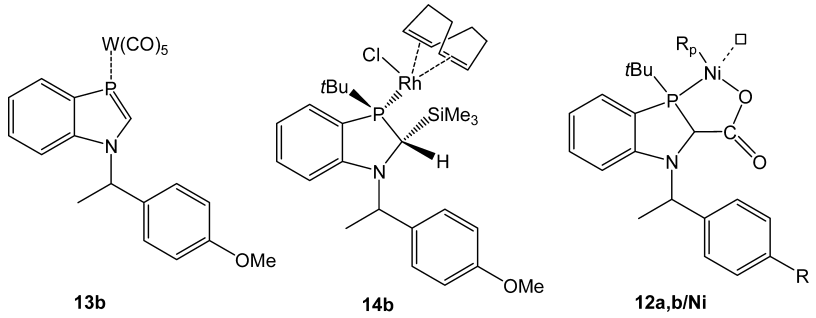
Chart 1. η^1P Coordination in 13b and 14b and Assumed $\hat{P}O^-$ Chelate Structure of the Ni−Ethylene Oligomerization Catalysts Formed from 12a,b and Ni(1,5-COD)$_2$[a]



[a]Legend: R_p, H or growing chain; □, coordination site for C_2H_4.

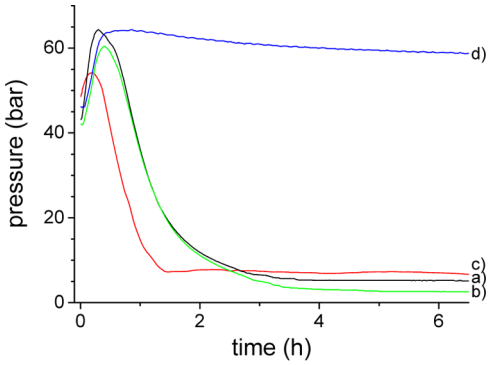


Figure 4. Ethylene consumption in the batch polymerization with catalysts generated in situ from Ni(COD)$_2$ and (a) **12a**, (b) **12b**, and (c) 1-neopentyl-3-*tert*-butyl-dihydrobenzazaphosphole-2-carboxylic acid,[6a] respectively, at 70 °C in THF. Curve d reflects the conversion in the presence of **12a**/**Ni** in THF/styrene (1:1).

mainly linear α-olefins. This selectivity corresponds well to that observed for catalysts formed from diphenylphosphinoacetic acid, phosphino ketones, and *o*-phosphinophenols, for which P,O$^-$ chelate structures were established.[20,21] Thus, this structure type can also be anticipated for the nickel catalysts generated with **12a,b** (Chart 1, right).

In comparison to nickel catalysts based on N-substituted diphenylphosphinoglycine[22] or 3-phenyl-1,3-azaphospholidine-2-carboxylic acid,[18] the efficiency of **12a,b**/Ni for ethylene conversion is improved. Therefore, and because incorporation of styrene comonomers into the CH_2 chain was observed for *o*-phosphinophenolate nickel catalysts,[23] we tested if copolymerization of ethylene with styrene is possible. The experiment with **12a**/Ni in THF/styrene (1:1 by volume) showed formation of a polymer at 70 °C, but with very slow consumption of ethylene (Figure 4). This could not be accelerated, since raising the temperature to 100 °C caused catalyst deactivation. According to the ^{1}H and ^{13}C NMR spectra the polymer consisted mainly of a mixture of a polystyrene (PS) and low-molecular-weight linear polyethylene with a phenyl to vinyl group ratio of roughly 7:1. The =CH proton signals for styryl end groups were very weak. Only trace signals for phenyl branching by incorporation of styrene into the polyethylene chain were detected by ^{13}C NMR (α- and β-C: δ 37.5, 28.2 ppm;[23] C_{br} superimposed by CH_2 signals of PS), in addition to very weak signals for methyl branching. The microstructure of the PS part (δ 41.5−41.8 (CH), 42.5−47.3 ppm (CH_2)) is complicated and was not analyzed. The molecular weight of the PE part was estimated by proton integration and correction for $CHCH_2$ of PS to about 750. Extraction of the polymer mixture with THF led to enrichment of the PS part (phenyl to vinyl group ratio 12.6:1) and lower M_{NMR} value of the PE part but not to full separation of the polymers. A GPC measurement of this extract using THF displayed a bimodal molecular weight distribution by a very broad shoulder at the low-molecular-weight side of the main curve.

CONCLUSIONS

Enantiomerically pure N chirally substituted 1,3-benzazaphospholes **4** are accessible via Pd-catalyzed C−N coupling of the corresponding chiral primary amines with *o*-dibromobenzene, subsequent C−P coupling with triethyl phosphite, reduction with $LiAlH_4$, and acid-catalyzed cyclization with $Me_2NCH(OMe)_2$. The reaction of **4** with *t*BuLi in Et_2O in the presence of KO*t*Bu leads to 2-CH lithiation and allows introduction of functional groups into this position, but the presence of an

Table 2. Oligomerization of Ethylene with Catalysts Formed from 12a,b[a]

entry	catalyst (amt, μmol)	amt of C_2H_4, g (mol); solvent (amt, mL)	C_2H_4 conversion, g (%); TON, (mol mol^{-1})	amt of polymer, g;[b] mp, °C; *D*, g cm^{-3}[c]	polymer: M_{NMR};[d] α-olefins (%), Me/C=C, %
1	**12a** (73), Ni(COD)$_2$ (73)	14.8 (0.53); THF (20)	14.8 (99); 7228	11.7; 110−114; 0.94	870; 87, 1.3
2	**12b** (75), Ni(COD)$_2$ (75)	15.9 (0.57); THF (20)	15.5 (97.5); 7368	11.6; 108−112; 0.94	900; 89, 1.3
3	**12b** (54), Ni(COD)$_2$ (54)	14.7 (0.52); THF (10), styrene (10)	7.9 (54); 5215[e]	6.8; 106−112; 0.94	750; 86, 1.6

[a]Conditions: batch oligo-/polymerization of ethylene in THF, p_{start} of C_2H_4 at room temperature 40−45 bar, start of conversion at ca. 70 °C. [b]Solid residue after flash distillation of volatiles, treatment with MeOH/aqueous concentrated HCl (1:1), washing with MeOH, and drying under vacuum. [c]Density of tablets of the solid (pressed at 10 kbar) determined by the sinking method in H_2O/EtOH. [d]M_{NMR} based on ^{1}H NMR integrals of CH_2 and CH_3 versus =CH protons in swollen polymers at 100 °C. [e]TON relative to C_2H_4 conversion.

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anisyl group causes competing additional directed lithiation in *o*-position of the methoxy group and subsequent additional functionalization of this position. Reaction of **4** with *t*BuLi in hexane/diethyl ether (without KO*t*Bu) proceeds with a strong preference, regiospecifically and with moderate diastereoselectivity versus the 1*S* carbon atom, for the "normal" addition product with *t*Bu at phosphorus and Li at C2. Quenching by methanol or highly diastereoselective trimethylsilylation showed that the addition at the P=C bond is moderately stereoselective under these conditions (2:1 molar ratio of diastereoisomers). Lithiation in toluene or hexane causes clean addition but partial or complete loss of diastereoselectivity. Trapping of the lithiodihydrobenzazaphospholes with CO_2 furnishes the respective carboxylic acids: however, with lower selectivity. These heterocyclic α-phosphino α-amino acids may slowly isomerize by their heteroacetalic nature and thus are unsuitable as ligands for asymmetric catalyses. However, the presence of the P−C−COOH structure unit allows the formation of nickel catalysts for the oligomerization of ethylene with the same selectivity as known from phosphinoacetate nickel catalysts, originally used in the first step of the SHOP process. The bulky P and N substituents induce high activity. This and each one of the examples of complexes of the chiral benzazaphospholes and P- and N-basic dihydrobenzazaphosphospholes provide the first information on the properties of these ligands and their potential for catalytic applications. This paves the way for further exploration of the use of these ligands in complex chemistry and catalysis.

EXPERIMENTAL SECTION

General Remarks. All operations were carried out under dry nitrogen or argon using Schlenk techniques and freshly distilled dry solvents. 1,2-Dibromobenzene, asymmetric amines, palladium salts, $Pd_2(dba)_3$ (tris(dibenzylideneacetone)dipalladium(0)), BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), DPPF (1,1′-bis-(diphenylphosphino)ferrocene), *t*BuLi solution, $ClSiMe_3$, $Ni(COD)_2$, and ethylene were purchased and used as received. NMR spectra were measured on an ARX300 multinuclear FT-NMR spectrometer (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Chemical shifts (δ) are given in ppm relative to Me_4Si or Me_4Si calibrated solvent signals and H_3PO_4 (85%), respectively. Assignment numbers follow the atom numbering of the nomenclature and are indicated in the Supporting Information. Coupling constants refer to J_{HH} in ^{1}H and J_{PC} in ^{13}C NMR data unless stated otherwise. The assignment of the ^{13}C NMR signals is based on 135-DEPT spectra, characteristic P−C coupling constants, and increment estimations. Low-resolution mass spectra were measured on an AMD40 single-focus mass spectrometer (Maurer) with EI (70 eV), and high-resolution mass spectra were obtained at the Institut für Organische Chemie, Universität Göttingen, using an APEX IV 7 T Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics) (ESI in MeOH, formic acid). Elemental analyses were performed with a MICRO CUBE CHN analyzer from Elementar vario under standard conditions.

2-Bromo-*N*-[(*S*)-1-phenylethyl]aniline (1a). A Schlenk flask was charged with 1,2-dibromobenzene (4.68 mL, 38.8 mmol), (*S*)-(−)-1-phenylethylamine (5.0 mL, 39.2 mmol), DPPF (1.61 g, 7.5 mol %), $Pd_2(dba)_3$ (1.78 g, 5 mol %), sodium 2-methylpropanolate (NaO*t*Bu; 5.2 g, 54 mmol), and toluene (40 mL). The mixture was heated for 6 h at 80 °C and then 20 h at 100 °C. Finally, the solvent was removed under vacuum, the residue was suspended in diethyl ether (40 mL), and the suspension was filtered through Celite. The brown-black filtrate was concentrated under vacuum and purified by column chromatography on silica gel using hexane/Et_2O (5%) for elution. Evaporation of the solvent furnished 6.42 g (60%) of a pale yellow viscous oil. ^{1}H NMR ($CDCl_3$): δ 1.57 (d, ^3J = 6.8 Hz, 3 H, CH_3), 4.51 (q, ^3J = 6.8 Hz, 1 H, NCH), 4.73 (br s, 1 H, NH), 6.38 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, 6-H), 6.49 (td, ^3J = 8.0, 7.2, ^4J = 1.5 Hz, 1 H, 4-H), 6.98 (td, ^3J = 8.1, 7.2, ^4J = 1.5 Hz, 1 H, 5-H), 7.19−7.35 (m, 5 H, phenyl-H), 7.40 (dd, ^3J = 7.9, ^4J = 1.5 Hz, 1 H, 3-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.10 (CH_3), 53.51 (NCH), 109.60 (C_q-2), 112.64 (C-6), 117.74 (C-4), 125.68 (2 C-*o*), 127.00 (C-*p*), 128.27 (C-5), 128.69 (2 C-*m*), 132.21 (C-3), 143.86, 144.46 (C_q-*i*, C_q-1). MS (20 °C): *m*/*z* (%) 277 (9) $[M + H]^+$, 276 (2), 275 (9) $[M + 1]^+$, 262 (13), 260 (14), 173 (18), 171 (19), 105 (100). HRMS (ESI in MeOH + FA): $C_{14}H_{14}BrN$ (276.17), calcd for $[M + H]^+$ 276.0382, 278.0362; found 276.0381, 278.0361.

2-Bromo-*N*-[(*S*)-1-(*p*-methoxyphenyl)ethyl]aniline (1b). Reaction of 1,2-dibromobenzene (4.08 mL, 33.8 mmol) with (*S*)-(−)-1-(4-methoxyphenyl)ethylamine (5.0 mL, 33.9 mmol) in the presence of DPPF (1.41 g, 7.5 mol %), $Pd_2(dba)_3$ (1.55 g, 5 mol %), and NaO*t*Bu (4.52 g, 47.0 mmol) in toluene (40 mL) and workup as described for **1a** (for elution hexane 92%/Et_2O 8%) gave 6.15 g (59%) of pale yellow viscous **1b**. Using the same procedure but with BINAP instead of DPPF provided 7.81 g (75%) of **1b**. ^{1}H NMR ($CDCl_3$): δ 1.55 (d, ^3J = 6.8 Hz, 3 H, CH_3), 3.78 (s, 3 H, OCH_3), 4.48 (q, ^3J = 6.8 Hz, 1 H, NCH), 4.82 (br s, 1 H, NH), 6.42 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, 6-H), 6.51 (td, ^3J = 7.8, 7.5, ^4J = 1.5 Hz, 1 H, 4-H), 6.85 (m, 2 H, *m*-H), 7.00 (td, ^3J = 8.1, 7.2, ^4J = 1.5 Hz, 1 H, 5-H), 7.25 (m, 2 H, *o*-H), 7.40 (dd, ^3J = 7.8, ^4J = 1.5 Hz, 1 H, 3-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.05 (CH_3), 53.04 (NCH), 55.23 (OCH_3), 109.72 (C_q-2), 112.87 (C-6), 114.06 (2 C-*m*), 117.83 (C-4), 126.81 (2 C-*o*), 128.27 (C-5), 132.22 (C-3), 136.36 (C_q-*i*), 143.81 (C_q-1), 158.60 (C_q-*p*). MS (20 °C): *m*/*z* (%) 307 (7) $[(^{81}Br)M]^+$, 305 (7) $[(^{79}Br)M]^+$, 291 (2), 210 (3), 136 (11), 135 (100), 134 (7). HRMS (ESI in MeOH + FA): $C_{15}H_{16}BrNO$ (306.20), calcd for $[M - H]^+$ 304.0332, 306.0316; found 304.0334, 306.0314; the $[M + H]^+$ peaks display low intensity.

2-Bromo-*N*-[(*S*)-1-(*p*-methylphenyl)ethyl]aniline (1c). Reaction of 1,2-dibromobenzene (3.12 mL, 21.2 mmol) with (*S*)-(−)-1-(4-methylphenyl)ethylamine (3.12 mL, 21.2 mmol) in the presence of DPPF (0.88 g, 7.5 mol %), $Pd_2(dba)_3$ (0.97 g, 5 mol %), and NaO*t*Bu (2.83 g, 29.4 mmol) in toluene (40 mL) and workup as described for **1a** (for elution hexane 98%/Et_2O 2%) gave 3.58 g (58%) of pale yellow viscous **1c**. ^{1}H NMR ($CDCl_3$): δ 1.57 (d, ^3J = 6.8 Hz, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 4.51 (q, ^3J = 6.8 Hz, 1 H, NCH), 4.72 (br s, 1 H, NH), 6.42 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, 6-H), 6.51 (td, ^3J = 8.1, 7.5, ^4J = 1.5 Hz, 1 H, 4-H), 7.00 (td, ^3J = 7.8, ^4J = 1.5 Hz, 1 H, 5-H), 7.14 (br d, ^3J = 7.8 Hz, 2 H, *o*- or *m*-H), 7.24 (br d, ^3J = 7.8 Hz, 2 H, *m*- or *o*-H), 7.40 (dd, ^3J = 7.5, ^4J = 1.5 Hz, 1 H, 3-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.90 (4-CH_3), 24.99 (CH_3), 53.07 (NCH), 109.44 (C_q-2), 112.48 (C-6), 117.49 (C-4), 125.46 (2 C-*o*), 128.13 (C-5), 129.24 (2 C-*m*), 132.03 (C-3), 136.39 (C_q-*p*), 141.35, 143.85 (C_q-*i*, C_q-1). MS (20 °C): *m*/*z* (%) 292 (1), 291 (8) $[(^{81}Br)M]^+$, 290 (2), 289 (9) $[(^{79}Br)M]^+$, 277 (8), 276 (9), 173 (10), 171 (11), 119 (100). HRMS (ESI in MeOH + FA): $C_{15}H_{16}BrN$ (290.20), calcd for $[(^{79}Br)M + Na]^+$ 312.0359; found 312.0358.

2-[(*S*)-(1-Phenylethyl)amino]benzenephosphonic Acid Diethyl Ester (2a). A Schlenk flask was charged with **1a** (6.0 g, 21.7 mmol), $P(OEt)_3$ (7.5 mL, 43.8 mmol), and $PdCl_2$ (0.23 g, 6 mol %), connected to a distillation apparatus that allows refluxing of $P(OEt)_3$ and distillation of EtBr, and heated under a slow stream of N_2 for ca. 2 h at 180−190 °C (bath). NMR samples were taken every 15−30 min to monitor the progress of the reaction and obtain optimal yields. Higher temperatures (>190 °C) led to dark mixtures and considerable decrease of the yields. The crude product was purified by column chromatography on silica gel using elution with hexane/EtOAc (14%). Removal of solvents provided 6.1 g (84%) of a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.34 (td, ^3J = 7.2, $^4J_{PH} \approx$ 1 Hz, 6 H, CH_3), 1.56 (d, ^3J = 6.6 Hz, 3 H, CH_3), 4.12 (m, 4 H, OCH_2), 4.50 (quin, ^3J = 6.2 Hz, 1 H, NCH), 6.42 (t, $^3J \approx {}^4J_{PH}$ = 8.1, 7.8 Hz, 1 H, 3-H), 6.60 (tdd, ^3J = 7.5, 7.2, $^4J_{PH}$ = 3.3, ^4J = 0.8 Hz, 1 H, 5-H), 7.13−7.37 (m, 7 H, NH, 4-H, phenyl-H), 7.45 (ddd, $^3J_{PH}$ = 14.8, ^3J = 7.8, ^4J = 1.5 Hz, 1 H, 6-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.25 (d, ^3J = 6.6 Hz, CH_3), 24.92 (s, CH_3), 53.19 (s, NCH), 62.00 (d, ^2J = 2.6 Hz, OCH_2), 107.99 (d, ^1J = 181.8 Hz, C_q-1), 112.59 (d, ^3J = 11.9 Hz, C-3), 115.67 (d, ^3J = 14.6 Hz, C-5), 125.75 (s, 2 C-*o*), 126.83 (s, C-*p*), 128.59 (s, 2 C-*m*), 133.33 (d, ^2J = 8.0 Hz, C-6), 133.91 (d, ^4J = 2.7 Hz, C-4), 144.83 (s, C_q-*i*),

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150.66 (d, ^2J = 9.3 Hz, C_q-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.7. MS (90 °C): m/z (%) 334 (28) $[M + 1]^+$, 392 (21), 319 (100). HRMS (ESI in MeOH + FA): $C_{18}H_{24}NO_3P$ (333.36), calcd for $[M + H]^+$ 334.1567; found 334.1565.

2-[(*S*)-(1-(*p*-Methoxyphenyl)ethyl)amino]-benzenephosphonic Acid Diethyl Ester (2b). Heating **1b** (6.0 g, 19.6 mmol) with $P(OEt)_3$ (6.86 mL, 40.0 mmol) and $PdCl_2$ (0.21 g, 6 mol %) and workup as described for **2a** gave 5.85 g (82%) of **2b** as a pale yellow viscous oil. ^1H NMR ($CDCl_3$): δ 1.21 (td, ^3J = 7.1, $^4J_{PH} \approx$ 1 Hz, 6 H, CH_3), 1.41 (d, ^3J = 6.4 Hz, 3 H, CH_3), 3.60 (s, 3 H, OCH_3), 3.99 (m, 4 H, OCH_2), 4.34 (quin, ^3J = 6.4 Hz, 1 H, NCH), 6.30 (br t, $^3J \approx {}^4J_{PH}$ = 8.1, 7.5 Hz, 1 H, 3-H), 6.45 (tdd, ^3J = 7.5, 7.3, $^4J_{PH}$ = 3.3, ^4J = 0.6 Hz, 1 H, 5-H), 6.70 (m, 2 H, *m*-H), 6.97 (br d, J = 5.7, 1 H, NH), 7.03 (br t, ^3J = 8.3, 7.3 Hz, 1 H, 4-H), 7.15 (m, 2 H, *o*-H), 7.44 (ddd, $^3J_{PH}$ = 14.8, ^3J = 7.6, ^4J = 1.7 Hz, 1 H, 6-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.00 (d, ^3J = 6.6 Hz, CH_3), 24.84 (s, CH_3), 52.05 (s, NCH), 54.81 (s, OCH_3), 61.67 (d, ^2J = 2.7 Hz, OCH_2), 107.45 (d, ^1J = 183.2 Hz, C_q-1), 112.12 (d, ^3J = 12.0 Hz, C-3), 113.69 (s, 2 C-*m*), 115.08 (d, ^3J = 13.3 Hz, C-5), 126.46 (s, 2 C-*o*), 133.05 (d, ^2J = 8.0 Hz, C-6), 133.65 (d, ^4J = 2.2 Hz, C-4), 136.74 (s, C_q-*i*), 150.71 (d, ^2J = 9.3 Hz, C_q-2), 158.18 (s, C_q-*p*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.8. MS (90 °C): m/z (%) 363 (8) $[M]^+$, 348 (26), 299 (14), 257 (16), 242 (100). HRMS (ESI in MeOH + FA): $C_{19}H_{26}NO_4P$ (363.39), calcd for $[M + H]^+$ 364.1672; found 364.1672; calcd for $[M + Na]^+$ 386.1492; found 386.1492.

2-[(*S*)-(1-(*p*-Methylphenyl)ethyl)amino]benzenephosphonic Acid Diethyl Ester (2c). Heating **1c** (4.42 g, 15.2 mmol) with $P(OEt)_3$ (5.14 mL, 4.98 g, 30.0 mmol) and $PdCl_2$ (0.16 g, 6 mol %) and workup as described for **2a** (elution with hexane/EtOAc (10%)) furnished 4.23 g (80%) of **2c** as a pale yellow oil. ^1H NMR ($CDCl_3$): δ 1.36 (td, ^3J = 7.1, $^4J_{PH} \approx$ 1 Hz, 6 H, CH_3), 1.56 (d, ^3J = 6.8 Hz, 3 H, CH_3), 2.32 (s, 3 H, *p*-CH_3), 4.13 (m, 4 H, OCH_2), 4.49 (quin, ^3J = 6.2 Hz, 1 H, NCH), 6.45 (t, $^3J \approx {}^4J_{PH} \approx$ 8.1, 7.5 Hz, 1 H, 3-H), 6.60 (tdd, ^3J = 7.5, 7.3, $^4J_{PH}$ = 3.3, ^4J = 0.9 Hz, 1 H, 5-H), 7.12 (m, 2 H, *o*- or *m*-H), 7.18 (tt, ^3J = 8.4, 7.2, $^4J \approx {}^5J_{PH} \approx$ 1.3 Hz, 1 H, 4-H), 7.26 (m, 2 H, *m*- or *o*-H), 7.46 (ddd, $^3J_{PH}$ = 14.7, ^3J = 7.7, ^4J = 1.7 Hz, 1 H, 6-H), 7.13 (br d, J = 7.6 Hz, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.21 (d, ^3J = 6.6 Hz, CH_3), 20.95 (s, *p*-CH_3), 24.92 (s, CH_3), 52.83 (s, NCH), 61.91 (d, ^2J = 4.0 Hz, OCH_2), 107.87 (d, ^1J = 183.1 Hz, C_q-1), 112.54 (d, ^3J = 11.9 Hz, C-3), 115.53 (d, ^3J = 14.6 Hz, C-5), 125.61 (s, 2 C-*o*), 129.22 (s, 2 C-*m*), 133.28 (d, ^2J = 7.7 Hz, C-6), 133.86 (br, C-4), 136.29 (s, C_q-*p*), 141.77 (s, C_q-*i*), 150.66 (d, ^2J = 9.3 Hz, C_q-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.8. MS (90 °C): m/z (%) 348 (3.0), 347 (12.1) $[M]^+$, 333 (9.3), 332 (41). HRMS (ESI in MeOH + FA): $C_{19}H_{26}NO_3P$ (347.39), calcd for $[M + H]^+$ 348.1723; found 348.1724.

***N*-[(*S*)-1-Phenylethyl]-2-phosphinoaniline (3a).** A solution of **2a** (5.0 g, 15.0 mmol) in Et_2O (20 mL) was added dropwise at −10 °C to $LiAlH_4$ pellets (1.71 g, 45.0 mmol) in Et_2O (150 mL). After it was stirred for 3 d at room temperature to complete the reduction, the mixture was cooled to ca. 10 °C, and water was added dropwise to decompose excess hydride. After the evolution of H_2 ceased, the addition of water was stopped (to avoid formation of a slurry), and the precipitate was filtered off and thoroughly washed with ether. The filtrate was dried over Na_2SO_4 and separated. Evaporation of the solvent gave 2.54 g (74%) of a pale yellow, highly air-sensitive oil. ^1H NMR ($CDCl_3$): δ 1.47 (d, ^3J = 6.8 Hz, 3 H, CH_3), 3.55 (d, $^1J_{PH}$ = 199.6 Hz, 2 H, PH_2), 4.40 (br s, NH superimposed with CH), 4.45 (q, ^3J = 6.8 Hz, 1 H, NCH), 6.28 (br d, ^3J = 8.3 Hz, 1 H, 6-H), 6.50 (tt, ^3J = 7.4, $^4J \approx {}^4J_{PH} \approx$ 1.2 Hz, 1 H, 4-H), 6.99 (tt, ^3J = 8.3, 7.8, $^4J \approx {}^5J_{PH} \approx$ 0.9 Hz, 1 H, 5-H), 7.06−7.26 (m, 5 H, phenyl-H), 7.38 (ddd, $^3J_{PH}$ = 12.4, ^3J = 7.5, ^4J = 1.7 Hz, 1 H, 3-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.15 (s, CH_3), 53.46 (s, NCH), 110.26 (d, ^1J = 10.6 Hz, C_q-2), 111.16 (s, C-6), 116.78 (d, ^3J = 11.9 Hz, C-4), 125.65 (s, 2 C-*o*), 126.92 (s, C-*p*), 128.64 (s, 2 C-*m*), 131.19 (s, C-5), 138.07 (d, ^2J = 33.2 Hz, C-3), 144.64 (s, C_q-*i*), 149.40 (s, C_q-1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −153.3. MS (90 °C): m/z (%) 230 (2), 229 (14) $[M]^+$, 214 (6), 125 (17), 105 (100). HRMS (ESI in MeOH + FA): $C_{14}H_{16}NP$ (229.26), calcd for $[M + H]^+$ 230.1093; found 230.1093.

***N*-[(*S*)-1-(*p*-Methoxyphenyl)ethyl]-2-phosphinoaniline (3b).** A solution of **2b** (5.0 g, 13.8 mmol) in Et_2O (20 mL) was reduced with $LiAlH_4$ (1.57 g, 41.3 mmol) in Et_2O (150 mL) and worked up as described for **3a**, yielding 2.61 g (73%) of a pale yellow, air-sensitive solid. Single crystals of **3b** were obtained at 0 °C from THF/hexane. Crystal data are compiled in Table S1 (Supporting Information) and selected bond lengths and angles in Figure 1. ^1H NMR ($CDCl_3$): δ 1.56 (d, ^3J = 6.6 Hz, 3 H, CH_3), 3.64 (d, $^1J_{PH}$ = 200.2 Hz, 2 H, PH_2), 3.77 (s, 3 H, OCH_3), 4.45 (br s, NH-superimposed with CH), 4.52 (q, ^3J = 6.6 Hz, 1 H, NCH), 6.40 (dt, ^3J = 8.3, $J \approx$ 1 Hz, 1 H, 6-H), 6.60 (tt, ^3J = 7.5, 7.2, $^4J \approx {}^4J_{PH} \approx$ 1.1 Hz, 1 H, 4-H), 6.85 (m, 2 H, *m*-H), 7.12 (tdd, ^3J = 8.3, 7.4, ^4J = 1.3, $^5J_{PH} \approx$ 0.6 Hz, 1 H, 5-H), 7.25 (m, 2 H, *o*-H), 7.48 (ddd, $^3J_{PH}$ = 12.5, ^3J = 7.4, ^4J = 1.3 Hz, 1 H, 3-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.20 (s, CH_3), 52.91 (s, OCH_3), 55.23 (s, NCH), 110.30 (d, ^1J = 10.6 Hz, C_q-2), 111.20 (s, C-6), 114.06 (s, 2 C-*m*), 116.73 (d, ^3J = 13.2 Hz, C-4), 126.77 (s, 2 C-*o*), 131.22 (s, C-5), 136.73 (s, C_q-*i*), 138.11 (d, ^2J = 33.2 Hz, C-3), 149.54 (s, C_q-1), 158.54 (s, C_q-*p*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −153.4. MS (90 °C): m/z (%) 260 (1.4), 259 (10) $[M]^+$, 244 (2), 153 (6), 136 (15), 135 (100). HRMS (ESI in MeOH + FA): calcd for $[M + H]^+$ 260.1199; found 260.1200. Anal. Calcd for $C_{15}H_{18}NOP$ (259.28): C, 69.48; H, 7.00; N, 5.40. Found C, 69.53; H, 7.02; N, 5.42.

***N*-[(*S*)-1-(*p*-Methylphenyl)ethyl]-2-phosphinoaniline (3c).** A solution of **2c** (3.9 g, 11.2 mmol) in Et_2O (20 mL) was reduced with $LiAlH_4$ (1.25 g, 33 mmol) in Et_2O (150 mL) and worked up as described for **3a** to give 2.01 g (74%) of pale yellow, air-sensitive **3c**. ^1H NMR ($CDCl_3$): δ 1.57 (d, ^3J = 6.4 Hz, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 3.66 (d, $^1J_{PH}$ = 200.2 Hz, 2 H, PH_2), 4.53 (q, ^3J = 6.6 Hz, 1 H, NCH), ca. 4.5 (vbr s, 1 H, NH superimposed with CH), 6.41 (d, ^3J = 8.3 Hz, 1 H, 6-H), 6.60 (br t, ^3J = 7.5, 7.2 Hz, 1 H, 4-H), 7.06−7.13 (superimposed m, 1 H, 5-H), 7.11 (m, 2 H, *o*- or *m*-H), 7.23 (m, 2 H, *m*- or *o*-H), 7.47 (ddd, $^3J_{PH}$ = 12.3, ^3J = 7.4, ^4J = 1.5 Hz, 1 H, 3-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.04 (s, *p*-CH_3), 25.06 (s, CH_3), 53.39 (s, NCH), 110.50 (d, ^1J = 4.0 Hz, C_q-2), 111.42 (d, ^3J = 2.7 Hz, C-6), 116.93 (d, ^3J = 10.6 Hz, C-4), 125.67 (s, 2 C-*o*), 129.36 (s, 2 C-*m*), 131.19 (s, C-5), 136.55 (s, C_q-*p*), 138.09 (d, ^2J = 33.1 Hz, C-3), 141.51 (s, C_q-*i*), 149.31 (s, C_q-1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −153.3. HRMS (ESI in MeOH + FA): $C_{15}H_{18}NP$ (243.28), calcd for $[M + H]^+$ 244.1250; found 244.1252.

1-[(*S*)-1-Phenylethyl]-1*H*-1,3-benzazaphosphole (4a). Excess dimethylformamide dimethylacetale (DMFA; 14.7 mL, 110 mmol) and $ClSiMe_3$ (1.5 mL, 11.8 mmol) were added to **3a** (2.50 g, 10.9 mmol). After this mixture was heated for 24 h at 50 °C, unconverted DMFA and $ClSiMe_3$ were evaporated under vacuum. The residue was dissolved in diethyl ether and treated with degassed 10% aqueous sulfuric acid at room temperature to extract N-basic impurities. The ether phase was washed with water, dried with Na_2SO_4, and separated. Removal of the solvent under vacuum provided 1.9 g (73%) of **4a** as a viscous oil. ^1H NMR ($CDCl_3$): δ 1.87 (d, ^3J = 6.8 Hz, 3 H, CH_3), 5.76 (q, ^3J = 6.8 Hz, 1 H, NCH), 7.00 (m, ^3J = 8.1 Hz, 2 H, *o*-H), 7.07 (tdd, ^3J = 7.9, 7.2, ^4J = 1.8, $^5J_{PH}$ = 0.9 Hz, 1 H, 5-H), 7.11−7.22 (superimposed m, 3 H, *m*-H, *p*-H), 7.20 (superimposed tt, ^3J = 8.1, 7.2, ^4J = 1.5, $^5J_{PH}$ = 0.9 Hz, 1 H, 6-H), 7.41 (br d, ^3J = 8.3 Hz, 1 H, 7-H), 8.01 (dddd, ^3J = 7.1, $^3J_{PH}$ = 4.2, ^4J = 1.5, ^5J = 0.6 Hz, 1 H, 4-H), 8.62 (d, $^2J_{PH}$ = 37.8 Hz, 1 H, 2-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.74 (s, CH_3), 57.78 (d, ^3J = 2.7 Hz, NCH), 113.10 (s, C-7), 120.22 (d, ^3J = 10.6 Hz, C-5), 124.59 (d, ^4J = 2.7 Hz, C-6), 125.86 (s, 2 C-*o*), 127.74 (s, C-*p*), 128.83 (s, 2 C-*m*), 129.46 (d, ^2J = 21.3 Hz, C-4), 141.38 (s, C_q-*i*), 142.49 (d, ^1J = 39.8 Hz, C_q-3a), 142.51 (d, ^2J = 5.3 Hz, C_q-7a), 157.58 (d, ^1J = 53.1 Hz, C-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 73.5. MS (80 °C): m/z (%) 240 (2), 239 (11) $[M]^+$, 163 (2), 148 (2), 135 (45), 105 (100). HRMS (ESI in MeOH + FA): $C_{15}H_{14}NP$ (239.25), calcd for $[M + H]^+$ 240.0937; found 240.0940.

1-[(*S*)-1-(*p*-Methoxyphenyl)ethyl]-1*H*-1,3-benzazaphosphole (4b). Reaction of **3b** (0.90 g, 3.47 mmol) with DMFA (4.6 mL, 34.4 mmol) in the presence of $ClSiMe_3$ (0.48 mL, 3.78 mmol) and workup as described for **4a** furnished 0.75 g (80%) of **4b** as a pale yellow solid. Single crystals were grown from a concentrated THF solution overlayered with hexane. Crystal data are compiled in Table S1

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(Supporting Information) and selected bond lengths and angles in Figure 2. ^{1}H NMR ($CDCl_3$): δ 1.93 (d, ^3J = 6.8 Hz, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 5.83 (q, ^3J = 6.9 Hz, 1 H, NCH), 6.82 (m, 2 H, *m*-H), 7.05 (m, 2 H, *o*-H), 7.16 (tm, ^3J = 7.9, 7.0, $^4J_{PH}$ = 1.9, ^4J = 1 Hz, 1 H, 5-H), 7.31 (tt, ^3J = 8.1, 7.2, $^4J \approx {}^5J_{PH}$ = 1.4 Hz, 1 H, 6-H), 7.54 (br d, ^3J = 8.1 Hz, 1 H, 7-H), 8.09 (ddd, ^3J = 8.1, $^3J_{PH}$ = 4.1, ^4J = 1.8, ^5J = 0.6 Hz, 1 H, 4-H), 8.65 (d, $^2J_{PH}$ = 37.8 Hz, 1 H, 2-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.64 (s, CH_3), 55.23 (s, OCH_3), 57.27 (d, ^3J = 2.7 Hz, NCH), 113.10 (s, C-7), 114.17 (s, 2 C-*m*), 120.19 (d, ^3J = 12.0 Hz, C-5), 124.56 (d, ^4J = 2.6 Hz, C-6), 127.27 (s, 2 C-*o*), 129.50 (d, ^2J = 21.3 Hz, C-4), 133.30 (s, C_q-*i*), 142.46 (d, ^2J = 5.4 Hz, C_q-7a), 142.58 (d, ^1J = 39.8 Hz, C_q-3a), 157.61 (d, ^1J = 53.1 Hz, C-2), 159.09 (s, C_q-*p*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 73.2. MS (90 °C): *m*/*z* (%) 269 (7) [*M*]$^+$, 163 (41), 148 (40), 135 (100). HRMS (ESI in MeOH+FA): calcd for [*M* + H]$^+$ 270.1042; found 270.1047; calcd for [*M* + Na]$^+$ 292.0862; found 292.0868. Anal. Calcd for $C_{16}H_{16}NOP$ (269.28): C, 71.37; H, 5.99; N, 5.20. Found: C, 71.58; H, 6.38; N, 5.51.

NMR Detection of Intermediate Phosphaalkene 5b and a Symmetric 1,3-Diphosphetane as Minor Side Products in the Synthesis of 4b without Catalyst. A mixture of **3b** (2.5 g, 9.64 mmol) and DMFA (1.55 mL, 11.6 mmol) was heated for 2 days at 50 °C. NMR monitoring displayed ^{31}P resonances at δ 73.2 (**4b**), 65.0 (*Z*-**5b**), 43.9 (*E*-**5b**), and −27.0 (1,3-diphosphetane), with relative intensities 55:5:20:25. After the mixture was heated for a further 3 days at 50 °C, unconverted DMFA was removed under vacuum and the crude product worked up as described for **4a** to give 2.1 g (81%) of **4b**. The NMR data of the latter are in good accordance with the values given above. The intermediate **5b** and the 1,3-diphosphetane side product were identified by characteristic proton NMR data. Data for **5b** are as follows. ^{1}H NMR ($CDCl_3$): δ 1.52 (d, ^3J = 6.6 Hz, 3 H, CH_3), 3.07 (d, $^4J_{PH}$ = 3.3 Hz, 6 H NMe_2), 3.78 (s, 3 H, OCH_3), 4.47 (superimposed q, $^3J \approx$ 6.4 Hz, 1 H, NCH), 6.06 (br d, 1 H, NH), 6.30 (br dd, ^3J = 7.8, ^4J = 2.8 Hz, 1 H, 6-H), 6.57 (td, ^3J = 7.4, ^4J = 1.0 Hz, 1 H, 4-H), 6.83 (superimposed m, 2 H, *m*-H), 6.97 (td, ^3J = 7.6, ^4J = 1.5 Hz, 1 H, 5-H), 7.27−7.32 (m, 3 H, *o*-H, 4-H), 8.80 (d, $^2J_{PH}$ = 13.9 Hz, 0.9 H, *E*-P═CH), 8.53 (d, $^2J_{PH}$ = 37.8 Hz, 0.1 H, *Z*-P═CH acyclic). Data for the 1,3-diphosphetane side product are as follows. ^{1}H NMR ($CDCl_3$): δ 1.51 (d, ^3J = 6.9 Hz, 6 H, CH_3), 2.42 (s, 12 H NMe_2), 3.77 (s, 6 H, OCH_3), 3.89 (t, $^2J_{PH}$ = 4.0 Hz, 2 H, P_2CH), 4.46 (superimposed q, $^3J \approx$ 6.4 Hz, 2 H, NCH), 5.03 (br t, $^3J \approx {}^4J_{PH} \approx$ 5.4 Hz, 2 H, NH), 6.35 (br d, $^3J \approx$ 7.5, 2 H, 6-H), 6.62 (superimposed br t, $^3J \approx$ 7.5 Hz, 2 H, 4-H), 6.83 (superimposed m, 4 H, *m*-H), 6.99 (superimposed t, $^3J \approx$ 7.5 Hz, 2 H, 5-H), 7.27−7.32 (m, 6 H, *o*-H, H-4). Evidence for the diphosphetane nature is given by the triplet at δ(^{1}H) 3.89 with small coupling to two P atoms, characteristic for symmetric 2,4-diamino-1,3-diphosphetanes.[24,25] For 2,4-bis-(dimethylamino)-1,3-diphenyl-1,3-diphosphetane, δ(^{1}H) 3.69 (t, $^2J_{PH}$ = 3.4 Hz), additional evidence was provided by crystal structure analysis.[24b]

1-[(*S*)-1-(*p*-Methylphenyl)ethyl]-1*H*-1,3-benzazaphosphole (4c). Reaction of **3c** (1.95 g, 8.02 mmol) with DMFA (10.7 mL, 80.2 mmol) in the presence of $ClSiMe_3$ (1.12 mL, 8.82 mmol) and workup as described for **4a** furnished 1.53 g (75%) of **4c** as a viscous oil. ^{1}H NMR ($CDCl_3$): δ 1.94 (d, ^3J = 7.2 Hz, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 5.83 (q, ^3J = 7.2 Hz, 1 H, NCH), 6.99 (m, 2 H, *o*- or *m*-H), 7.09 (m, 2 H, *m*- or *o*-H), 7.15 (tdd, ^3J = 8.1, 7.2, $^4J_{PH}$ = 1.9, ^4J = 0.9 Hz, 1 H, 5-H), 7.30 (tt, ^3J = 8.3, 7.2, $^4J \approx {}^5J_{PH} \approx$ 1.4 Hz, 1 H, 6-H), 7.52 (br d, ^3J = 8.1 Hz, 1 H, 7-H), 8.09 (dddd, ^3J = 8.1, $^3J_{PH}$ = 4.2, ^4J = 1.1, ^5J = 0.7 Hz, 1 H, 4-H), 8.68 (d, $^2J_{PH}$ = 37.8 Hz, 1 H, 2-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.00 (s, CH_3), 21.71 (s, CH_3), 57.59 (d, ^3J = 2.7 Hz, NCH), 113.13 (s, C-7), 120.19 (d, ^3J = 11.9 Hz, C-5), 124.58 (d, ^4J = 2.7 Hz, C-6), 125.89 (s, 2 C-*o*), 129.48 (d, ^2J = 21.3 Hz, C-4), 129.52 (s, 2 C-*m*), 137.53, 138.38 (2s, C_q-*p*, C_q-*i*), 142.53 (d, ^2J = 5.3 Hz, C_q-7a), 142.54 (d, ^1J = 39.8 Hz, C_q-3a), 157.63 (d, ^1J = 53.1 Hz, C-2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 73.1. HRMS (ESI in MeOH + FA): $C_{16}H_{16}NP$ (253.28), calcd for [*M* + H]$^+$ 254.1093; found 254.1097.

Detection of 1-[(*S*)-1-(*p*-Methoxyphenyl)ethyl]-2-(trimethylsilyl)-1*H*-1,3-benzazaphosphole (7b) and 1-[(*S*)-1-(4-Methoxy-3-(trimethylsilyl)phenyl)ethyl]-2-(trimethylsilyl)-1*H*-1,3-benzazaphosphole (7d). A solution of *t*BuLi in hexane (0.15 mL, 0.24 mmol) was added dropwise at −70 °C to a mixture of **4b** (43 mg, 0.16 mmol) and KO*t*Bu (21.3 mg, 0.19 mmol) in Et_2O (10 mL). Stirring was continued while the mixture was warmed slowly to −30 °C (5 h). Then it was cooled again to −70 °C, $ClSiMe_3$ (0.03 mL, 0.24 mmol) was added, and the mixture was warmed to room temperature. After the mixture was stirred overnight, volatile components were removed under vacuum. The residue was extracted with diethyl ether and the solvent removed from the filtrate, affording 41 mg of a pale yellow oil. This was identified by NMR and mass spectrometric data as a mixture of **7b** (65 mol %) and **7d** (20 mol %) and small amounts of residual **4b** (6 mol %) and diastereoisomeric addition products **10b** (4 + 5 mol %). The NMR data of **4b** and **10b** are in accordance with those given above and below, respectively. Data for **7b** are as follows. ^{1}H NMR ($CDCl_3$): δ 0.49 (d, $^4J_{PH}$ = 1.5 Hz, 9 H, $SiMe_3$), 2.04 (d, ^3J = 7.2 Hz, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 6.03 (q, ^3J = 7.2 Hz, 1 H, NCH), 6.72 (d, ^3J = 8.3 Hz, 1 H, 7-H), 6.85 ($m_{AA'}$, 2 H, *o*- or *m*-H), 7.01−7.21 (m, *m*- or *o*-H, 5-H, 6-H, 7-H), 8.02−8.08 (m, 4-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.40 (d, ^3J = 8.0 Hz, $SiMe_3$), 17.71 (s, CH_3), 55.22 (s, OCH_3), 60.70 (135DEPT d, ^3J = 2.2 Hz, NCH), 114.10 (s, 2 C-*m*), 116.10 (s, C-7), 119.37 (d, ^3J = 10.6 Hz, C-5), 124.10 (d, ^4J = 2.7 Hz, C-6), 127.04 (s, 2 C-*o*), 129.02 (d, ^2J = 19.9 Hz, C-4), 132.17 (s, C_q-*i*), 144.66 (d, ^2J = 4.0 Hz, C_q-7a), 144.79 (d, ^1J = 42.5 Hz, C_q-3a), 158.79 (s, C_q-*p*), 180.84 (d, ^1J = 73.0 Hz, C_q-2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 117.9. HRMS (ESI in MeOH + FA): $C_{19}H_{24}NOPSi$ (341.46), calcd for [*M* + H]$^+$ 342.1438; found 342.1440. Data for **7d** are as follows. ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 9 H, 3′-$SiMe_3$), 3.77 (s, 3 H, OCH_3), 6.72 (d, ^3J = 8.1 Hz, 5′-H); $SiMe_3$ doublet, MeCH, and aryl signals superimposed by those of **7b**. ^{13}C{^{1}H} NMR ($CDCl_3$): δ −1.05 (s, $SiMe_3$), 0.44 (d, ^3J = 9.3 Hz, $SiMe_3$), 17.86 (s, CH_3), 55.04 (s, OCH_3), 60.94 (135DEPT s, NCH), 109.51 (s, C-5′), 113.11 (s, C_q-3′), 116.19 (s, C-7), 119.28 (d, ^3J = 10.6 Hz, C-5), 124.01 (d, ^4J = 2.6 Hz, C-6), 128.46 (s, C-6′), 128.95 (d, ^2J = 21.2 Hz, C-4), 131.49 (s, C_q-1′), 132.17 (superimposed s, C-2′), 144.77 (d, ^2J = 4 Hz, C_q-7a), ca. 144.8 (d, C_q-3a, noise level), 164.89 (s, C_q-4′), 180.81 (d, ^1J = 73 Hz, C_q-2, noise level). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 117.5. MS (90 °C): *m*/*z* (%) 414 (0.8) [M^+ (**7d**)], 342.5 (0.7), 341.6 (3) [M^+ (**7b**)], 327 (1), 235 (2), 207 (12), 164 (2), 147 (7), 135 (100).

Detection of 1-[(*S*)-1-(*p*-Methoxyphenyl)ethyl]-1*H*-1,3-benzazaphosphole-2-carboxylic Acid (8b) and 1-[(*S*)-1-(3-Carboxy-4-methoxyphenyl)ethyl]-1*H*-1,3-benzazaphosphole-2-carboxylic Acid (8d). A solution of *t*BuLi in hexane (0.33 mL, 0.53 mmol) was added dropwise at −70 °C to a mixture of **4b** (94 mg, 0.35 mmol) and KO*t*Bu (47 mg, 0.42 mmol) in diethyl ether (20 mL). Stirring was continued while the mixture was warmed slowly to −30 °C (5 h). Then it was cooled again to −70 °C and a slow stream of dry CO_2 bubbled in over 40 min (color change from orange to yellow). The mixture was warmed slowly to room temperature overnight. $ClSiMe_3$ (0.07 mL, 0.55 mmol) was added at −70 °C, and the mixture was stirred with warming to room temperature and filtered. Removal of the solvent provided a pale yellow solid, which was treated with excess MeOH (20 mL) for desilylation. MeOH and Me_3SiOMe were removed under vacuum, the residue was dissolved in diethyl ether, and N-basic impurities were extracted with degassed 10% aqueous H_2SO_4. The ether phase was washed with water and dried over Na_2SO_4. Removal of ether under vacuum furnished 81 mg of a yellow solid, identified by conclusive NMR data as a mixture of **8b** (34 mol %, 25 mg) and **8d** (66 mol %, 56 mg). Data for **8b** are as follows. ^{1}H NMR (600 MHz, d_8-THF): δ 1.94 (d, ^3J = 7.2 Hz, 3 H, CH_3), 3.72 (s, 3 H, OCH_3), 6.82 ($m_{AA'}$, 2 H, *m*-H), 7.00 (superimposed $m_{BB'}$ and q, 3 H, *o*-H, NCH), 7.05 (superimposed tt, 1 H, 5-H), 7.13 (br t, ^3J = 8.4, 7.2 Hz, 1 H, 6-H), 8.00 (dd, ^3J = 7.8, $^3J_{PH}$ = 4.8 Hz, 1 H, 4-H); 7-H superimposed by signals of **8d** in the range 7.24−7.31. ^{13}C{^{1}H} NMR (CD_3OD): δ 17.55 (s, CH_3), 55.63 (s, OCH_3), 56.96 (d, ^3J = 4.0 Hz, NCH), 114.93 (s, 2 C-*m*), 118.06 (s, C-7), 121.43 (d, ^3J = 13 Hz, C-5), 127.15 (d, ^4J = 2.7 Hz, C-6), 128.42 (s, 2 C-*o*), 130.71 (d, ^2J = 22.6 Hz, C-4), 134.06 (s, C_q-*i*), 145.31 (d, ^2J = 7.5 Hz, C_q-7a), 160.21 (s, C_q-*p*); C_q-3a, C_q-2 and COOH doublets at noise level. ^{31}P{^{1}H} NMR (CD_3OD): δ 122.05. Data for **8d** are as follows. ^{1}H NMR (600 MHz, d_8-THF): δ 1.97 (d, ^3J = 7.2 Hz, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 7.07 (superimposed m, 1 H, 5-H), 7.08 (superimposed d, $^3J \approx$ 8 Hz, 1 H,

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5′-H), 7.17 (t, ^3J = 8.4 Hz, 1 H, 6-H), 7.23 (ddd, ^3J = 8.4, ^4J = 2.4, J = 0.6 Hz, 1 H, 6′-H), 7.29 (superimposed d ($^3J \approx 8.4$ Hz) and q, 2 H, 7-H, NCH), 7.76 (dd, ^4J = 2.4, ^5J = 0.7 Hz, 1 H, 2′-H), 8.02 (dd, ^3J = 7.8, $^3J_{PH}$ = 4.2 Hz, 1 H, 4-H). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 17.44 (s, CH_3), 56.53 (s, OCH_3), 56.54 (superimposed d, ^3J = 2.7 Hz, NCH), 113.60 (s, C-5′), 117.75 (s, C-7), 120.86 (s, C_q-3′), 121.58 (d, ^3J = 13.3 Hz, C-5), 127.46 (d, ^4J = 4.0 Hz, C-6), 130.47 (s, C-6′), 130.89 (d, ^2J = 22.5 Hz, C-4), 133.20 (s, C-2′), 134.18 (s, C_q-1′), 143.92 (d, ^1J = 37.1 Hz, C_q-3a), 145.21 (d, ^2J = 7.9 Hz, C_q-7a), 159.57 (s, C_q-4′), 162.70 (d, ^1J = 53.1 Hz, C_q-2), 166.82 (d, ^2J = 22.6 Hz, 2-COOH), 169.40 (s, 3′-COOH). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 123.4.

(3*S*/3*R*)-3-*tert*-Butyl-1-[(1*S*)-1-(*p*-methoxyphenyl)ethyl]-2,3-dihydro-1*H*-1,3-benzazaphosphole (10b). A solution of *t*BuLi in hexane (0.58 mL, 0.93 mmol) was added dropwise at −70 °C to **4b** (164 mg, 0.61 mmol) in Et_2O/hexane (each 5 mL). The mixture was warmed slowly to −30 °C (5 h). The resulting orange-red solution of the lithium reagent was then quenched at −70 °C with methanol (10 mL). After the mixture was warmed to room temperature, the solvents were removed under vacuum. Diethyl ether was added to the residue, the insoluble part was filtered off, and ether was removed under vacuum to give 159 mg of a pale yellow oil. NMR and HRMS data indicate two diastereoisomers of **10b**, A:B 58:29 mol % (by integration of methyl protons), and 13 mol % of unconverted **4b**: calcd yield of **10b** 142 mg, 71%. ^1H NMR (C_6D_6): δ 0.88 (d, $^3J_{PH}$ = 12.1 Hz, 9 H, CMe_{3B}), 0.97 (d, $^3J_{PH}$ = 12.1 Hz, 9 H, CMe_{3A}), 1.13 (d, ^3J = 6.8 Hz, 3 H, CH_{3B}), 1.33 (d, ^3J = 7.2 Hz, 3 H, CH_{3A}), 3.06 (dd, ^2J = 12.6, $^2J_{PH}$ = 3.6 Hz, 1 H, $PCH_{cis\ to\ tBu\text{-}B}$), 3.21 (superimposed dd, ^2J = 12.9, $^2J_{PH}$ = 22 Hz, 1 H, $PCH_{trans\text{-}B\ or\ A}$), 3.29 (superimposed dd, ^2J = 12.9, $^2J_{PH}$ = 22.8 Hz, 1 H, $PCH_{trans\text{-}A\ or\ B}$), 3.29 (s, 3 H, OCH_{3A}), 3.31 (s, 3 H, OCH_{3B}), 3.42 (d, ^2J = 12.6, $^2J_{PH}$ = 3.6 Hz, 1 H, $PCH_{cis\text{-}A}$), 4.70 (superimposed q, $^3J \approx 7$ Hz, 1 H, NCH_A), 4.71 (superimposed q, $^3J \approx 7$ Hz, 1 H, NCH_B), 6.42 (br d, ^3J = 7.9 Hz, 1 H, 7-H_A), 6.47 (br d, ^3J = 8.3 Hz, 1 H, 7-H_B), 6.66 (m, 2 H, *m*-H_A), 6.62−6.75 (superimposed m, 2 H, 5-H_{AB}), 6.79 (m, 2 H, *m*-H_B), 6.97 (m, 2 H, *o*-H_A), 7.13 (m, superimposed, 2 H, *o*-H_B), 7.10−7.23 (superimposed m, 6-H_{AB}), 7.40−7.47 (superimposed m, 4-H_{AB}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.50 (s, CH_{3B}), 18.43 (s, CH_{3A}), 27.08 (superimposed d, ^2J = 15.9 Hz, CMe_{3A}), 27.38 (superimposed d, ^2J = 14.6 Hz, CMe_{3B}), 30.91 (d, ^1J = 18.6 Hz, CMe_{3B}), 31.13 (d, ^1J = 19.9 Hz, CMe_{3A}), 42.92 (d, ^1J = 21.2 Hz, PCH_{2B}), 43.43 (d, ^1J = 21.2 Hz, PCH_{2A}), 54.07 (s, NCH_A), 54.42 (s, NCH_B), 55.40 (s, OCH_{3AB}), 108.82 (s, C-7_A), 108.94 (s, C-7_B), 114.67 (s, 2 C-m_B), 114.81 (s, 2 C-m_A), 117.35 (d, ^3J = 6.6 Hz, C-5_A), 117.83 (d, ^3J = 8.0 Hz, C-5_B), 124.61 (d, ^1J = 11.9 Hz, C_q-3a_A), 125.50 (d, ^1J = 13.3 Hz, C_q-3a_B), 128.97 (135DEPT s, 2 C-o_A), 129.68 (s, 2 C-o_B), 131.43 (br s, C-6_A and C-6_B), 133.30 (d, ^2J = 22.6 Hz, C-4_A), 133.39 (d, ^2J = 21.2 Hz, C-4_B), 134.03 (s, C_q-i_A), 134.61 (s, C_q-i_B), 155.20 (br s, C_q-7a_A), 155.32 (br s, C_q-7a_B), 159.78 (s, C_q-p_A), 160.00 (s, C_q-p_B). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −13.4 (B), −14.0 (A). HRMS (ESI in MeOH + FA): $C_{20}H_{26}NOP$ (327.40), calcd for $[M + H]^+$ 328.1825; found 328.1825.

3-*tert*-Butyl-1-[(1*S*)-1-phenylethyl]-2-(trimethylsilyl)-2,3-dihydro-1*H*-1,3-benzazaphosphole (11a). $ClSiMe_3$ (38 μL, 0.30 mmol) was added to **4a** (45.5 mg, 0.19 mmol) in Et_2O/hexane (5 mL each), followed by addition of a solution of *t*BuLi in hexane (0.18 mL, 0.29 mmol) at −70 °C. The mixture was slowly warmed to room temperature, stirred overnight, filtered, and washed with ether. Removal of the solvent under vacuum gave 50 mg (71%) of a pale yellow oil, containing two diastereoisomers A and B of **11a**, molar ratio 65:35% (by integration of Me protons). ^1H NMR (C_6D_6): δ 0.078 (d, $^4J_{PH}$ = 1.1 Hz, 9 H, $SiMe_{3A}$), 0.085 (d, $^4J_{PH}$ = 1.1 Hz, 9 H, $SiMe_{3B}$), 0.90 (d, $^3J_{PH}$ = 12.1 Hz, 9 H, CMe_{3A}), 0.93 (d, $^3J_{PH}$ = 11.7 Hz, 9 H, CMe_{3B}), 1.52 (d, ^3J = 7.2 Hz, 3 H, CH_{3A}), 1.53 (d, ^3J = 7.2 Hz, 3 H, CH_{3B}), 3.22 (d, $^2J_{PH}$ = 4.2 Hz, 1 H, $PCH_{cis\text{-}B}$), 3.58 (d, $^2J_{PH}$ = 4.9 Hz, 1 H, $PCH_{cis\text{-}A}$), 4.23, 4.45 (2 superimposed q, 2 H, $NCH_{A,B}$), 6.22 (superimposed d, ^3J > 8.1 Hz, 1 H, 7-H_B), 6.25 (d br, ^3J > 7.9 Hz, 1 H, 7-H_A), 6.57 (superimposed tdd, ^3J = 7.2, $^4J_{PH}$ = 2.3, ^4J = 1 Hz, 1 H, 5-H_B), 6.61 (superimposed tdd, ^3J = 7.2, $^4J_{PH}$ = 2.3, ^4J = 1 Hz, 1 H, 5-H_A), 6.87 (td, ^3J = 8.3, 7.2, ^4J = 1.5 Hz, 1 H, 6-H_B), 6.99 (td, ^3J = 8.3, 7.2, ^4J = 1.5 Hz, 1 H, 6-H_A), 7.02−7.35 (m, phenyl-H_{AB}), 7.40 (superimposed ddd, ^3J = 7.6, $^3J_{PH}$ = 4.9, ^4J = 1 Hz, 1 H, 4-H_B), 7.42 (superimposed ddd, ^3J = 7.6, $^3J_{PH}$ = 4.9, ^4J = 1 Hz, 1 H, 4-H_A). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −1.56 (d, ^3J = 8.0 Hz, $SiMe_{3B}$), −0.73 (d, ^3J = 9.3 Hz, $SiMe_{3A}$), 16.30 (s, CH_{3B}), 20.34 (s, CH_{3A}), 26.76 (d, ^2J = 15.9 Hz, CMe_{3A}), 26.90 (d, ^2J = 15.9 Hz, CMe_{3B}), 31.64 (d, ^1J = 27.8 Hz, CMe_{3A}), 31.93 (d, ^1J = 29.2 Hz, CMe_{3B}), 48.83 (d, ^1J = 43.8 Hz, PCH_A), 53.90 (d, ^1J = 43.8 Hz, PCH_B), 58.76 (d, ^3J = 2.7 Hz, NCH_A), 60.91 (d, ^3J = 4.0 Hz, NCH_B), 110.05 (s, C-7_A), 112.58 (s, C-7_B), 117.03 (d, ^3J = 6.6 Hz, C-5_B), 117.24 (d, ^3J = 8.0 Hz, C-5_A), 123.69 (d, ^1J = 10.6 Hz, C_q-3a_A), 125.22 (d, ^1J = 13.3 Hz, C_q-3a_B), 127.40 (s, C-p_B), 127.53 (s, 2 C-o_B), 127.60 (s, 2 C-o_A), 127.68 (s, C-p_A), 129.25 (s, 2 C-m_A), 129.33 (s, 2 CH-m_B), 130.32 (s, C-6_B), 131.39 (s, C-6_A), 132.45 (d, ^2J = 22.5 Hz, C-4_A), 132.86 (d, ^2J = 22.6 Hz, C-4_B), 143.84 (s, C_q-i_B), 144.81 (s, C_q-i_A), 153.00 (s, C_q-7a_B), 155.97 (s, C_q-7a_A). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −4.6, −5.3 (intensity ratio 65:35%). MS (210 °C): *m*/*z* (%) 370.5 (0.5) [M^+], 343 (0.9), 264 (4), 208 (12), 136 (15), 135 (100). HRMS (ESI in MeOH + FA): $C_{22}H_{32}NPSi$ (369.56), calcd for $[M + H]^+$ 370.2114; found 370.2119.

3-*tert*-Butyl-1-[(1*S*)-1-(*p*-methoxyphenyl)ethyl]-2-(trimethylsilyl)-2,3-dihydro-1*H*-1,3-benzazaphosphole (11b). $ClSiMe_3$ (30 μL, 0.24 mmol) was added to **4b** (45.8 mg, 0.17 mmol) in Et_2O/hexane (5 mL each), followed by addition of a solution of *t*BuLi in hexane (0.16 mL, 0.26 mmol) at −70 °C. The mixture was worked up as described for **11a** to give 50 mg (73%) of a pale yellow oil, containing two diastereoisomers A and B of **11b**, molar ratio 62:38% (by integration of Me protons). ^1H NMR (C_6D_6): δ 0.10 (d, $^4J_{PH}$ = 1.1 Hz, 9 H, $SiMe_{3A}$), 0.13 (d, $^4J_{PH}$ = 1.1 Hz, 9 H, $SiMe_{3B}$), 0.92 (d, $^3J_{PH}$ = 12.1 Hz, 9 H, CMe_{3A}), 0.94 (d, $^3J_{PH}$ = 11.7 Hz, 9 H, CMe_{3B}), 1.53 (d, ^3J = 7.2 Hz, 3 H, CH_{3A}), 1.54 (d, ^3J = 7.2 Hz, 3 H, CH_{3B}), 3.25 (d, $^2J_{PH}$ = 4.2 Hz, 1 H, $PCH_{cis\text{-}B}$), 3.305 (s, 3 H, OCH_{3A}), 3.313 (s, 3 H, OCH_{3B}), 3.60 (d, $^2J_{PH}$ = 4.5 Hz, 1 H, $PCH_{cis\text{-}A}$), 4.44 (q, ^3J = 6.8 Hz, 1 H, NCH_B), 4.45 (q, ^3J = 6.9 Hz, 1 H, NCH_A), 6.28 (d br, ^3J = 8.3 Hz, 1 H, 7-H_B), 6.32 (d br, ^3J = 8.3 Hz, 1 H, 7-H_A), 6.58 (superimposed tdd, ^3J = 7.2, $^4J_{PH}$ = 2.2, ^4J = 1.1 Hz, 1 H, 5-H_B), 6.63 (superimposed tdd, ^3J = 7.2, $^4J_{PH}$ = 2.2, ^4J = 1.1 Hz, 1 H, 5-H_A), 6.78 (m, 2 H, *m*-CH_A), 6.79 (m, 2 H, *m*-CH_B), 6.92 (ddd, ^3J = 8.4, 7.1, ^4J = 1.5 Hz, 1 H, 6-H_B), 7.04 (ddd, ^3J = 8.3, 7.2, ^4J = 1.1 Hz, 1 H, 6-H_A), 7.17 (superimposed m, 2 H, *o*-CH_A), 7.24 (m, 2 H, *o*-CH_B), 7.38−7.46 (m, 2 H, 4-H_{AB}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −1.51 (d, ^3J = 8.0 Hz, $SiMe_{3B}$), −0.69 (d, ^3J = 9.3 Hz, $SiMe_{3A}$), 16.28 (s, CH_{3B}), 20.42 (s, CH_{3A}), 26.77 (d, ^2J = 14.6 Hz, CMe_{3A}), 26.92 (d, ^2J = 15.9 Hz, CMe_{3B}), 31.67 (d, ^1J = 29.2 Hz, CMe_{3A}), 31.94 (d, ^1J = 27.9 Hz, CMe_{3B}), 48.82 (d, ^1J = 43.7 Hz, PCH_A), 53.71 (d, ^1J = 43.8 Hz, PCH_B), 55.42 (s, OCH_{3AB}), 58.23 (d, ^3J = 2.7 Hz, NCH_A), 60.35 (d, ^3J = 4.0 Hz, NCH_B), 110.03 (s, C-7_A), 112.52 (s, C-7_B), 114.69 (s, C-m_A), 114.79 (s, C-m_B), 116.94 (d, ^3J = 8.0 Hz, C-5_B), 117.12 (d, ^3J = 6.6 Hz, C-5_A), 123.68 (d, ^1J = 11.9 Hz, C_q-3a_A), 125.20 (d, ^1J = 13.3 Hz, C_q-3a_B), 128.64 (135DEPT s, C-o_B), 128.70 (135DEPT s, C-o_A), 130.32 (s, C-6_B), 131.37 (s, C-6_A), 132.47 (d, ^2J = 22.6 Hz, C-4_A), 132.86 (d, ^2J = 22.6 Hz, C-4_B), 135.50 (s, C_q-i_B), 136.54 (s, C_q-i_A), 153.10 (s, C_q-7a_B), 156.04 (s, C_q-7a_A), 159.52 (s, C_q-p_B), 159.77 (s, C_q-p_A). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −4.7, −5.2 (intensity ratio 60:40%). MS (210 °C): *m*/*z* (%) 399.5 (0.5) [M^+], 343 (1), 264 (4), 208 (12), 136 (15), 135 (100).

3-*tert*-Butyl-1-[(1*S*)-1-phenylethyl]-2,3-dihydro-1*H*-1,3-benzazaphosphole-2-carboxylic Acid (12a). A solution of *t*BuLi in hexane (0.60 mL, 0.96 mmol) was added dropwise at −70 °C to **4a** (154 mg, 0.65 mmol) in Et_2O/hexane (each 10 mL). After slow warming to −30 °C (5 h), a stream of CO_2 was introduced at −70 °C for 20 min (color change from orange-red to yellow). The mixture was warmed slowly to room temperature overnight and cooled again to −70 °C, and $ClSiMe_3$ (0.13 mL, 1.02 mmol) was added. After it was warmed to room temperature, the mixture was filtered, the residue was washed with ether, and the solvent was removed under vacuum, yielding a yellow solid. Treatment with methanol (5 mL) and evaporation of the solvent and $MeOSiMe_3$ under vacuum furnished 160 mg of a yellow solid. The NMR spectra displayed three diastereoisomers of **12a** in a A:B:C ratio of 41:31:20 and traces of the two diastereoisomers of **10a**, identified by characteristic phosphorus resonances ($\delta(^{31}P)$ −12.8, −12.2) similar to those of **10b** (see above): corrected yield of **12a** 150 mg (67%). NMR data of the major diastereoisomers A and B (most signals of C are

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superimposed) are as follows. ^{1}H NMR (CD_3OD): δ 0.81 (d, $^3J_{PH}$ = 12.6 Hz, 9 H, CMe_{3B}), 0.98 (d, $^3J_{PH}$ = 12.6 Hz, 9 H, CMe_{3A}), 1.59 (d, ^3J = 7.2 Hz, 3 H, CH_{3B}), 1.60 (d, ^3J = 6.8 Hz, 3 H, CH_{3A}), 4.30 (d, $^2J_{PH}$ = 2.6 Hz, 1 H, $PCH_{cis\text{-}B}$), 4.54 (d, $^2J_{PH}$ = 2.6 Hz, 1 H, $PCH_{cis\text{-}A}$), 4.69 (br q, ^3J = 6.8 Hz, 1 H, NCH_B), 4.97 (br q, ^3J = 7.2 Hz, 1 H, NCH_A), 6.54 (br d, ^3J = 8.1 Hz, 1 H, 7-H_B), 6.57 (br d, ^3J = 8.3 Hz, 1 H, 7-H_A), 6.62 (superimposed tdd, ^3J = 7.5, $^4J_{PH}$ = 2.7, ^4J = 1 Hz, 5-H_B) 6.65 (superimposed tdd, ^3J = 7.5, $^4J_{PH}$ = 2.4, ^4J = 1 Hz, 5-H_A), 7.12 (td, ^3J = 7.8, 7.5, ^4J = 1.5 Hz, 6-H_A), 7.19 (td, ^3J = 8.3, 7.5, ^4J = 1.5 Hz, 6-H_B), 7.23−7.41 (phenyl-H, 4-H). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 19.08 (superimposed s, CH_{3A}), 19.11 (sh, CH_{3B}), 26.34 (d, ^2J = 15.9 Hz, CMe_{3A}), 26.48 (d, ^2J = 15.9 Hz, CMe_{3B}), 31.92 (d, ^1J = 22.6 Hz, CMe_{3B}), 32.08 (d, ^1J = 22.6 Hz, CMe_{3A}), 57.60 (s, NCH_C), 58.02 (s, NCH_B), 58.58 (s, NCH_A), 61.06 (d, ^1J = 26.6 Hz, PCH_B), 61.35 (d, ^1J = 27.8 Hz, PCH_A), 66.41 (d, ^1J = 29.1 Hz, PCH_C), 109.90 (s, C-7_A), 110.15 (s, C-7_B), 117.97 (d, ^3J = 8.0 Hz, C-5_A), 119.13 (d, ^3J = 8.0 Hz, C-5_B), 122.54 (d, ^1J = 11.9 Hz, C_q-$3a_A$), 124.91 (d, ^1J = 11.9 Hz, C_q-$3a_B$), [127.18, 128.05, 128.43, 128.51 (2C), 128.65, 129.33 (2C), 129.49 (2C), 129.60 (2C) (phenyl-$CH_{A\text{-}C}$)], 131.39 (s, C-6_B), 131.53 (s, C-6_A), 132.14 (d, ^2J = 21.3 Hz, C-4_A), 132.43 (d, ^2J = 21.2 Hz, C-4_B), 143.05 (s, C_q-i_B), 143.10 (s, C_q-i_A), 155.32 (s, C_q-$7a_B$), 155.48 (s, C_q-$7a_A$), 177.29 (d, ^2J = 15.9 Hz, COO_A), 178.01 (d, ^2J = 15.9 Hz, COO_B). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 18.1, 17.8, 8.5 (relative intensities 41:31:20%). HRMS (ESI in MeOH + FA): $C_{20}H_{24}NO_2P$ (341.38), calcd for $[M + H]^+$ 342.1617; found 342.1628.

3-*tert*-Butyl-1-[(1*S*)-1-(*p*-methoxyphenyl)ethyl]-2,3-dihydro-1*H*-1,3-benzazaphosphole-2-carboxylic Acid (12b). Compound **4b** (127 mg, 0.47 mmol) in Et_2O/hexane (10 mL each) was lithiated with *t*BuLi in hexane (0.44 mL, 0.70 mmol), treated with CO_2 and then with $ClSiMe_3$ (0.10 mL, 0.79 mmol), and worked up as described for **12a** to give 128 mg of a yellow solid. The NMR spectra indicated two major diastereoisomers of **12b** with $\delta(^{31}P)$ (d_8-THF) 15.4, 15.1 and intensity ratio of ca. 60:40% and a trace amount of *t*BuCOOH. Flash column chromatography on silica gel using hexane (98%)/ethyl acetate (2%) after several weeks furnished 97 mg (55%) of pure **12b**, but with a changed diastereoisomer distribution, $\delta(^{31}P)$ (CD_3OD) 17.9, 17.4, 11.7, 8.5 and intensity ratio 18:53:2:27%, assigned to B, A, D, and C by similar intensity ratios (*t*Bu proton integrals 19:52:4:25) and characteristic ^{1}H and ^{13}C NMR data, respectively. Data after column chromatography are as follows. ^{1}H NMR (CD_3OD): δ 0.79 (d, $^3J_{PH}$ = 12.5 Hz, 9 H, CMe_{3B}), 0.98 (d, $^3J_{PH}$ = 12.5 Hz, 9 H, CMe_{3A}), 1.04 (d, $^3J_{PH}$ = 11.7 Hz, CMe_{3D}), 1.05 (d, $^3J_{PH}$ = 12.1 Hz, 9 H, CMe_{3C}), 1.46 (d, ^3J = 6.8 Hz, 3 H, CH_{3C}), 1.55 (d, ^3J = 6.8 Hz, 3 H, CH_{3A}), 1.57 (d, ^3J = 7.2 Hz, 3 H, CH_{3B}), 1.60 (d, ^3J = 7.2 Hz, CH_{3D}), 3.74 (s, OCH_{3D}), 3.76 (s, 3 H, OCH_{3B}), 3.77 (s, 3 H, OCH_{3A}), 3.78 (s, 3 H, OCH_{3C}), 4.23 (d, $^2J_{PH}$ = 2.6 Hz, 1 H, $PCH_{cis\text{-}B}$), 4.47 (d, $^2J_{PH}$ = 2.6 Hz, 1 H, $PCH_{cis\text{-}A}$), 4.66 (d, $^2J_{PH}$ = 7.6 Hz, 1 H, $PCH_{trans\text{-}C}$), 4.64 (q, ^3J = 7.2 Hz, 1 H, NCH_B), 4.92 (q, ^3J = 7.2 Hz, 1 H, NCH_A), 4.94 (q, ^3J = 7.2 Hz, 1 H, NCH_B), 6.20 (br d, ^3J = 8.3 Hz, 1 H, 7-H_C), 6.35 (br d, ^3J = 8.3 Hz, 1 H, 7-H_D), 6.61 (superimposed br d, ^3J = 8.3 Hz, 1 H, 7-H_{AB}), 6.59−6.69 (superimposed m, 5-H), 6.85 (m, 2 H, *m*-CH_A), 6.87 (superimposed m, 2 H, *m*-CH_B), 6.89 (superimposed m, 2 H, *m*-CH_C), 6.98−7.27 (superimposed m, 6-H, 4-H), 7.30 (m, 2 H, *o*-H_B), 7.40 (m, 2 H, *o*-H_A), 7.47 (m, *o*-H_D), 7.60 (m, d fine splitting J_{PH} = 0.9 Hz, 2 H, *o*-H_C). ^{13}C NMR (CD_3OD): δ 11.09 (s, CH_{3C}), 18.51 (s, CH_{3A}), 18.85 (s, CH_{3B}), 26.37 (d, ^2J = 15.9 Hz, CMe_{3A}), 26.43 (d, ^2J = 15 Hz, CMe_{3B}), 27.34 (d, ^2J = 15.9 Hz, CMe_{3C}), 27.54 (superimposed d, ^2J = 15 Hz, CMe_{3D}), 31.92 (d, ^1J = 22.5 Hz, CMe_{3B}), 32.09 (d, ^1J = 22.5 Hz, CMe_{3A}), 33.25 (d, ^1J = 26.5 Hz, CMe_{3C}), 55.64 (br s, OCH_{3AC}), 55.70 (s, OCH_{3B}), 57.23 (s, NCH_A), 57.29 (s, NCH_D), 57.37 (s, NCH_B), 57.40 (s, NCH_C), 60.89 (d, ^1J = 27.9 Hz, PCH_B), 61.21 (d, ^1J = 27.9 Hz, PCH_A), 66.36 (d, ^1J = 29.2 Hz, PCH_C), 109.68 (s, C-7_A), 109.90 (s, C-7_B), 113.19 (s, C-7_C), 114.60 (s, 2 C-m_{AC}), 114.84 (s, 2 C-m_B), 117.83 (two superimposed d, ^3J = 8.0 Hz, C-5_{AB}), 119.05 (d, ^3J = 8.0 Hz, C-5_C), 122.48 (d, ^1J = 11.9 Hz, C_q-$3a_{AC}$), 124.85 (d, ^1J = 13.3 Hz, C_q-$3a_B$), 129.21 (s, C-6_A), 129.75 (s, 2 C-o_B), 131.02 (s, 2 C-o_A), 131.60 (s, 2 C-o_C), 130.70 (s, C-6_C), 131.44 (s, C-6_B), 132.22 (d, ^2J = 22.6 Hz, C-4_A), 132.34 (d, ^2J = 22.6 Hz, C-4_B), 132.86 (d, ^2J = 22.6 Hz, C-4_C), 134.40 (s, C_q-i_A), 134.71 (s, C_q-i_B), 135.50 (s, C_q-i_C), 154.88 (d, ^2J = 2.7 Hz, C_q-$7a_C$), 155.3 (sh, C_q-$7a_B$), 155.37 (s, C_q-$7a_A$), 160.01 (s, C_q-p_C), 160.54 (s, C_q-p_A), 160.63 (s, C_q-p_B), 173.41 (br s, COO_C), 177.31 (d, ^2J = 15.9 Hz, COO_A), 178.24 (d, ^2J = 15.9 Hz, COO_B); tentative diastereoisomer assignment by intensity ratios. HRMS (ESI in MeOH + FA): $C_{21}H_{26}NO_3P$ (371.41), calcd for $[M + H]^+$ 372.1723; found 372.1719.

{η^1*P*-1-[(1*S*)-1-(*p*-methoxyphenyl)ethyl]-1*H*-1,3-benzazaphosphole}pentacarbonyltungsten(0) (13b). A solution of $W(CO)_5(THF)$ was generated by UV irradiation of $W(CO)_6$ (161 mg, 0.458 mmol) in THF (85 mL) at 20 °C for 2.5 h using a water-cooled 250 W medium-pressure mercury UV lamp. Neat **4b** (110.9 mg, 0.412 mmol) was added, the solution was stirred for 1 day at room temperature, and the solvent was removed under vacuum. Diethyl ether was added to the residue, the soluble part was separated by filtration, and the solvent was evaporated under vacuum, yielding 168 mg (69%) of a very air sensitive pale brown viscous product. ^{1}H NMR (CD_3OD): δ 1.98 (d, ^3J = 6.8 Hz, 3 H, CH_3), 3.72 (s, 3 H, OCH_3), 6.08 (q, ^3J = 6.8 Hz, 1 H, CH), 6.85 ($m_{AA'}$, 2 H, *m*-CH), 7.17 ($m_{BB'}$, 2 H, *o*-CH), 7.26 (tdd, ^3J = 7.9, 7.0, $^4J_{PH}$ = 2.8, ^4J = 0.9 Hz, 1 H, 5-H), 7.4 (ddt, ^3J = 8.6, 7.1, ^4J = $^5J_{PH}$ = 1.5 Hz, 1 H, 6-H), 7.83 (br d, ^3J = 8.7 Hz, 1 H, 7-H), 7.98 (tt, $^3J \approx {}^3J_{PH}$ = 8.1, 7.8, $^4J \approx {}^5J$ = 1.2, 0.9 Hz, 1 H, 4-H), 8.91 (d, $^2J_{PH}$ = 32.9 Hz, 1 H, 2-H). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 21.51 (s, CH_3), 55.28 (s, OCH_3), 57.19 (s, CH), 114.85 (s, 2 C-*m*), 115.53 (d, ^3J = 4 Hz, C-7), 122.04 (d, ^3J = 15.9 Hz, C-5), 126.73 (d, ^4J = 4 Hz, C-6), 127.70 (d, ^2J = 13.3 Hz, C-4), 128.07 (s, 2 C-*o*), 133.77 (d, ^4J = 2.7 Hz, C_q-*i*), 138.66 (d, ^1J = 22.5 Hz, C_q-3a), 143.82 (s, C_q-7a), 153.73 (d, ^1J = 27.9 Hz, C-2), 160.46 (s, C_q-*p*), 195.45 (d, ^2J = 9.3 Hz, 4 *cis*-CO), 200.17 (d, ^2J = 29.2 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 33.8 (satellite d, $^1J_{PW}$ = 242.6 Hz). MS (90 °C): *m*/*z* (%) 593 (1) $[M^+]$, 377 (0.6), 352 (4), 268 (11), 135 (100). HRMS (ESI in MeOH): $C_{21}H_{16}NO_6PW$ (593.17), calcd for $[M(^{184}W) + OH]^+$ 610.0249; found 610.0249; calcd for $[M(^{184}W) + ONa]^+$ 632.0069; found 632.0067. The detection of the $[M + OH]^+$ and $[M + ONa]^+$ peaks, both with correct isotopic patterns, indicates the high air sensitivity of **13b** in solution. IR (KBr): ν_{CO} 2076 (wm), 1924 (vs) cm^{-1}.

Detection of {η^1*P*-3-*tert*-butyl-1-[(1*S*)-1-(*p*-methoxyphenyl)-ethyl]-2-(trimethylsilyl)-2,3-dihydro-1*H*-1,3-benzazaphosphole}(1,5-octadiene)rhodium Chloride (14b). A solution of $[Rh(COD)Cl]_2$ (39 mg, 0.079 mmol) in THF (8 mL) was added slowly at −30 °C to a solution of **11b** (63 mg, 0.16 mmol) in THF (5 mL). After the mixture was stirred for 2 days at room temperature, the solvent was removed, the orange-brown residue was extracted with diethyl ether, and the solvent was removed under vacuum to give 79 mg of a diastereoisomer mixture (A:B:C by ^{31}P signal integration ca. 60:35:5) of **14b**, contaminated with a small amount of unconverted $[Rh(COD)Cl]_2$. ^{1}H NMR (C_6D_6): δ 0.43 (s, 9 H, $SiMe_{3A}$), 0.65 (s, 9 H, $SiMe_{3B}$), 0.91 (d, ^3J = 7.5 Hz, 3 H, CH_{3A}), 0.95 (d, ^3J = 7.2 Hz, 3 H, CH_{3B}), 1.41 (d, $^3J_{PH}$ = 13.6 Hz, 9 H, $PCMe_{3A}$), 1.50 (d, $^3J_{PH}$ = 14.0 Hz, 9 H, $PCMe_{3B}$), 1.55−1.80, 2.00−2.30 (m br, 8 H, $CH_{2A,B}$), 3.27 (s, 3 H, OCH_{3B}), 3.28 (s, 3 H, OCH_{3A}), 3.83 (m br, 1 H, $=CH_B$), 4.13 (m br, 1 H, $=CH_A$), 4.32 (m br, 1 H, $=CH_{A,B}$), 4.30 (superimposed d, $^2J_{PH}$ = 12.5 Hz, PCH_B), 4.44 (q, ^3J = 6.8 Hz, 1 H, NCH_A), 4.55 (d, $^2J_{PH}$ = 11.0 Hz, 1 H, PCH_A), 4.57 (q, ^3J = 6.6 Hz, 1 H, NCH_B), 5.46 (m br, 2 H, $=CH_B$), 5.68 (m br, 2 H, $=CH_A$), 6.33 (br d, ^3J = 8 Hz, 1 H, H-7_B), 6.48 (br d, ^3J = 8.3 Hz, 1 H, H-7_A), 6.45 (tdd, ^3J = 7.5, 7.2, $^4J_{PH}$ = 2.6, ^4J = 0.9 Hz, 1 H, H-5_B), 6.54 (tdd, ^3J = 7.5, 7.2, $^4J_{PH}$ = 2.7, ^4J = 0.9 Hz, 1 H, H-5_A), 6.76 ($m_{AA'}$, 2 H, CH-$m_{A,B}$), 7.06 (ddt, ^3J = 8.3, 7, $^4J \approx {}^5J_{PH}$ = 1.3 Hz, 1 H, H-6_A), 7.00−712 (superimposed m, H-$4_{A,B}$), 7.12 (ddt, ^3J = 8.3, 7, $^4J \approx {}^5J_{PH}$ = 1.3 Hz, 1 H, H-6_B), 7.23 ($m_{BB'}$, 2 H, CH-o_B), 7.25 ($m_{BB'}$, 2 H, CH-o_A). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.54 (d, ^3J = 2.7 Hz, 2-$SiMe_3A$), 3.76 (d, ^3J = 2.7 Hz, 2 $SiMe_{3B}$), 19.71 (s, CH_{3B}), 23.49 (s, CH_{3A}), 28.57 (s, CH_{2A}), 29.31 (br s, CH_{2B}), 29.54 (d, J = 2.2 Hz, CH_{2B}), 30.03 (br s, CH_{2A}), 30.65 (d, ^2J = 5.6 Hz, $PCMe_{3A}$), 30.86 (d, ^2J = 5.3 Hz, $PCMe_{3B}$), 33.57, (DEPT d, J = 2 Hz, CH_{2A}), 33.90 (d, J = 3 Hz, CH_{2B}), 34.23 (d, J = 2 Hz, CH_{2B}), 34.47 (d, J = 3.3 Hz, CH_{2A}), 37.20 (d, ^1J = 8 Hz, $PCMe_{3B}$), 38.07 (d, ^1J = 5 Hz, $PCMe_{3A}$), 51.87 (s, OCH_{3A}), 54.03 (s, OCH_{3B}), 55.48 (d, ^1J = 11.9 Hz, $PCH_{A,B}$), 59.52 (d, ^3J = 3 Hz, NCH_B), 60.57 (s, NCH_A), 65.86 (d, $^1J_{RhC}$ = 13.3 Hz, $=CH_A$), 68.75 (d, $^1J_{RhC}$ = 13.3 Hz, $=CH_B$), 69.89 (d, $^1J_{RhC}$ = 13.3 Hz,

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=CH_B), 71.10 (d, $^1J_{RhC}$ = 13.3 Hz, =CH_A), 101.78 (DEPT dd, J = 14.3, 7.7 Hz, =CH_A), 102.72 (dd, J = 13, 7 Hz, =CH_B), 104.31 (superimposed m, =$CH_{A,B}$), 112.08 (d, ^3J = 4.0 Hz, C-7_A), 113.91 (d, ^3J = 4 Hz, C-7_B), 115.02 (s, 2 C-$m_{A,B}$), 118.00 (d, ^3J = 9 Hz, C-5_A), 118.31 (d, ^3J = 8 Hz, C-5_B), 121.0 (dd, ^1J = 33 Hz, C_q-$3a_A$; C_q-$3a_B$ at noise level), 128.72 (DEPT s, 2 C-o_B), 130.74 (s, 2 C-o_A), 131.41 (br s, C-6_B), 131.68 (d, ^2J = 9.3 Hz, C-4_B), 131.73 (d, ^2J = 9.3 Hz, C-4_A), 132.40 (br s, C-6_A), 135.08 (s, C_q-i_A), 136.19 (s, C_q-i_B), 154.69 (d, ^3J = 2.7 Hz, C_q-$7a_B$), 155.49 (d, ^3J = 2.7 Hz, C_q-$7a_A$), 159.82 (s, C_q-p_B), 160.45 (s, C_q-p_A). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.5 (d, $^1J_{RhP}$ = 151.1 Hz, A), 34.9 (d, $^1J_{RhP}$ = 151.1 Hz, B), 35.35 (d, $^1J_{RhP}$ = 151.9 Hz, C), integral ratio 60:35:5.

Crystal Structure Analysis of 3b and 4b. Crystals of **3b** and **4b** were mounted on glass fibers in inert oil. Data were recorded at 100 K on an Oxford Diffraction Xcalibur E diffractometer using Mo Kα radiation (λ = 0.71073 Å). Crystal data are summarized in Table S1 (Supporting Information). The structures were refined by full-matrix least squares on F^2.[27] Hydrogen atoms of NH and PH_2 groups were refined freely (but for the latter with a P−H distance restraint), methyls were refined as idealized rigid groups allowed to rotate but not tip, and other H atoms were included using a riding model starting from calculated positions.

Ethylene Oligomerization/Polymerization. Solution of **12a** and **12b**, respectively, in THF (10 mL) were added to a solution of $Ni(COD)_2$ in cold THF (10 mL) (for quantities see Table 2), and the mixtures were transferred into the autoclave. This was then pressurized with ethylene. After control of weight and tightness, heating to 70 °C and pressure registration were started. After 15 h the autoclave was cooled to about 10 °C, residual ethylene was released through a cooling trap, the contents of the autoclave were transferred to a flask, and the volatiles were flash distilled. The density was determined from polymer disks, pressurized at 10 kbar by the sinking method in EtOH/water (with detergent); the NMR spectra were measured in C_6D_5Br at 100 °C after swelling for 1 day at 100 °C. Further details of the working technique have been described earlier.[26]

■ ASSOCIATED CONTENT

Supporting Information

A table, figures, and CIF files giving experimental and spectroscopic data for the new compounds and crystallographic data for **3b** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC files 975110 and 975111 also contain crystallographic data for **3b** and **4b**.

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Notes

The authors declare no competing financial interest.

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