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The Synthesis, Structure and Properties of Diazaphospholes: Reagents and Ligands for Asymmetric Synthesis

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Abstract: Reaction of C_2 diamines with PCl_3 and Et_3N in toluene, followed by water or hydrogen sulfide, gave a series of cyclic phosphorous acid diamides (diazaphosphole oxides) and thiophosphorous acid diamides (diazaphosphole sulfides), respectively. Similarly, reaction of diamines with phenyl dichlorophosphine gave phenyl diazaphospholes. The synthesis, properties, and structure of these diazaphospholes are reported.

Introduction

We recently began to explore methods for the asymmetric synthesis of α hydroxy phosphonic acid derivatives (phosphonamides and phosphonates).[1] Hydroxy phosphonic acid derivatives are most easily prepared *via* the addition of a dialkyl phosphite to an aldehyde (the Pudovik reaction),[2] and we therefore sought to develop an asymmetric variant of the Pudovik reaction employing a homochiral phosphite equivalent.[3] The ideal chiral auxiliary for this purpose would possess C_2 stereochemistry. The C_2 symmetry would avoid the formation of an additional stereocenter at phosphorus during reagent formation, and thus alleviate any problems associated with diastereoisomer separation. In the choice of auxiliary, we were encouraged by literature precedent to examine the formation of cyclic phosphorous acid diamides (diazaphosphole oxides) derived from C_2 diamines.[4] Several useful C_2 diamines are readily available, easily resolved and N-alkylated,[5] and the α-carbanions of related homochiral phosphonamides were known exhibit a large diastereofacial bias upon reaction with electrophiles.[6] Moreover, Modro and others had demonstrated the ease of P-alkylation of $(Me_2N)_2P(O)H$ and $(Et_2N)_2P(O)H$, and these results suggested that anion formation and alkylation should be possible with more complex diamides.[7] Furthermore, the P-H moiety allows access to a wide variety of reaction manifolds,[8] including, anion formation via deprotonation of the P-H bond, Pd-catalyzed arylation and vinylation, and oxidation to the corresponding chloro derivatives. In addition, it became apparent that a similar concept and synthetic strategy could be applied to the synthesis of novel ligands for metal complex formation.[9] Herein we report, in full, the results of our study on the preparation, structure, and reactions of diazaphospholes as potential asymmetric phosphonylating agents and ligands for metal complexation.

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Results

The disubstituted diamines **1a-f** were prepared by the reductive alkylation of racemic or homochiral[5a,b] *trans*-1,2-cyclohexanediamine. Addition of aldehydes to the 1,2-cyclohexanediamine in methanol gave the corresponding bis-imine, which was reduced in *situ* with sodium borohydride to give the diamines **1a-f**. Attempts to prepare the isopropyl substituted diamine **1g** *via* bis-imine formation with acetone resulted in monoalkylation. However, direct alkylation with isopropyl iodide in a refluxing two-phase mixture of PhMe and aq. $NaHCO_3$ allowed access to the desired diamine **1g**. Racemic N,N'-diphenyl-1,2-diaminocyclohexane **1h**,[5c] and the racemic N-benzyl substituted derivatives of 2,3-butanediamine **3i** and stilbene diamine **3j**[5d] were prepared by literature methods. The disubstituted diamines **1a-j** were converted to dihydrochloride salts which were easily recrystallized to analytical purity, and provided a convenient form for storage. The optical purity of diamines **1a-g** was determined by ^1H NMR spectroscopy of the diastereoisomeric salts formed in *situ* with (+)-Mosher's acid.[10] The presence of signals for only one diastereoisomer indicated that the 1,2-diaminocyclohexane had been resolved to >99% optical purity.

Scheme 1

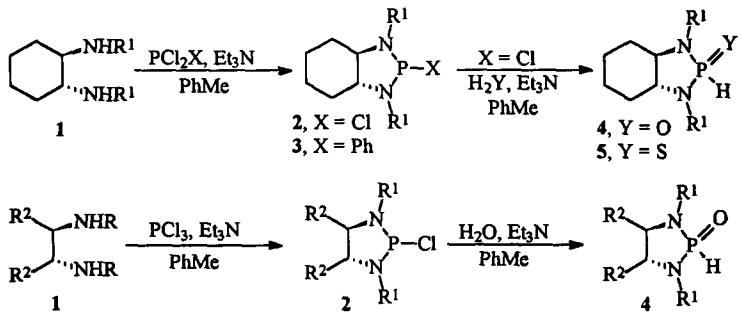


Table 1. Phosphorous Acid Diamides (Diazaphosphole oxides and sulfides)

Diamine	R^2	R^1	X	Product	Yield(%)	^{31}P, δ, ppm	m.p. (°C)
1a	1,2-cyclohexyl	$PhCH_2$	O	**4a**	80	19.9	129-131
2c	1,2-cyclohexyl	2-CH_3-$C_6H_4CH_2$	O	**4b**	85	22.3	oil
1c	1,2-cyclohexyl	2,4,6-$(CH_3)_3$-$C_6H_2CH_2$	O	**4c**	62	17.7	173-178
1d	1,2-cyclohexyl	1-NaphthCH_2	O	**4d**	93	22.7	waxy solid
1e	1,2-cyclohexyl	$(CH_3)_3CCH_2$	O	**4e**	90	32.9	100-102
1f	1,2-cyclohexyl	$(CH_3)_2CH(CH_2)_2$	O	**4f**	63	21.5	oil
1g	1,2-cyclohexyl	$(CH_3)_2CH$	O	**4g**	54	10.4	liquid
1h	1,2-cyclohexyl	Ph	O	**4h**	95	13.3	waxy solid
1i	Me	$PhCH_2$	O	**4i**	62	14.8	108.5-110
1j	Ph	$PhCH_2$	O	**4j**	97	15.1	134.5-136
1a	1,2-cyclohexyl	$PhCH_2$	S	**5a**	40	62.6	122-123.5
1e	1,2-cyclohexyl	$(CH_3)_3CCH_2$	S	**5eb**	67	70.7	93.5-94.5

Condensation of the diamines **1a-j** with PCl_3 and Et_3N in toluene solution, followed by filtration of the resulting $Et_3N.HCl$, gave the crude chloro-diazaphospholes **2a-j**. Addition of one equivalent of water and one equivalent of Et_3N to the toluene solution of the chloro-diazaphospholes **2** gave the phosphorous acid diamides

(diazaphosphole oxides) **4** (Table 1). Alternatively, addition of hydrogen sulfide to a toluene solution of chlorides **2a** and **2e** yielded the corresponding thiophosphorous acid diamides (diazaphosphole sulfides) **5a** and **5e**, respectively. The crude diazaphosphole oxides were purified either by trituration with diethyl ether, column chromatography on silica gel, or recrystallization from ethyl acetate in good yield (Table 1). Using a similar procedure, the diamines **1a** and **1e** were condensed with phenyl dichlorophosphine to give the phenyl-diazaphospholes **3a** and **3e**, respectively (Table 2).[11]

Table 2. Phenyl Diazaphospholes

Diamine	R^2	R^1	Y	Product	Yield(%)	^{31}P, δ, ppm	m.p. (°C)
1a	1,2-cyclohexyl	$PhCH_2$	Ph	**3a**	91	101.9	oil
1e	1,2-cyclohexyl	$(CH_3)_3CCH_2$	Ph	**3e**	84	119.1	119.5 - 120

In the general, the diazaphosphole oxides **4** were solids and proved to be quite stable to storage. However, the liquid diazaphosphole oxides **4g** and **4h**, and diazaphosphole sulfides **5** decomposed on storage, presumably by hydrolysis or oxidation. The ^{31}P NMR resonances for the diazaphosphole oxides were in the range δ 13-33 ppm, whereas, the sulfides **5a** and **5e** were approximately 40 ppm downfield from the corresponding oxides **4a** and **4e** at 62.5 and 70.6 ppm, respectively. The monocyclic butanediamine derivative **4i** and stilbene diamine derivative **4j** showed phosphorus resonances upfield of the corresponding bicyclic system **4a**.

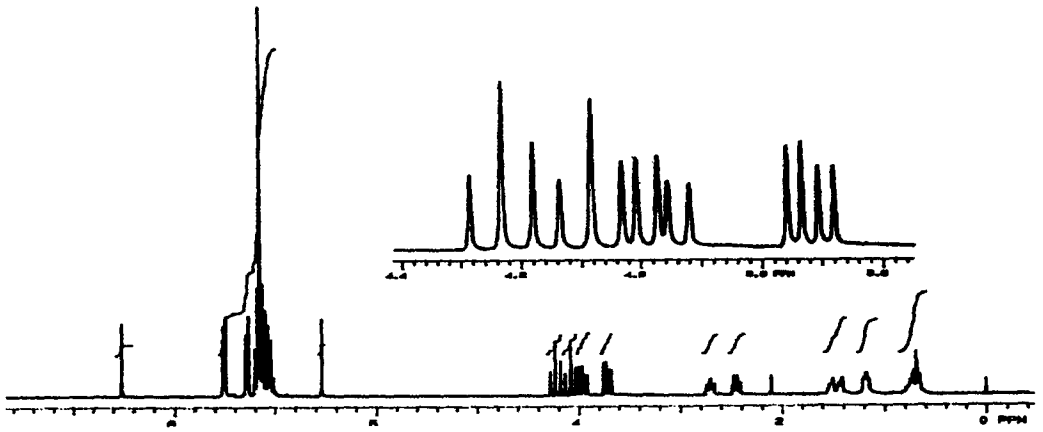


Figure 1. ^1H NMR Spectrum of Diazaphosphole Oxide **4a**

The ^1H NMR spectra of diazaphosphole oxides **4** displayed some interesting characteristics. The proton attached to phosphorus appeared as a charateristic doublet in the range 6.5 to 8.0 ppm, with a $^1J_{PH}$ value of 550 to 600 Hz. The ^1H NMR spectrum of the benzyl substituted diamine **1a** illustrates the characteristics typical of the C_2 diamines **1** studied. The four N-benzylic protons are diastereotopic (pairs) and appear as an AB quartet at δ 3.66 ($\Delta\nu_{AB}$ = 62 Hz, J_{AB} = 13.4 Hz). However, in the ^1H NMR spectrum of the diazaphosphole oxide **4a** (Figure 1), the four benzylic protons are unique and exhibit P-H couplings ($^3J_{PH}$), and consequently appear as two doublets of doublets and two apparent triplets (each integrating to one proton). The cyclohexyl methine protons are also split into two multiplets, in contrast to one multiplet in the parent diamine. The ^1H NMR spectra of the phenyl diazaphosphole **3a** show similar coupling patterns for the benzylic and methine protons.[11]

In the reactions of the diazaphosphole oxides with aldehydes,[1] and in the catalytic chemistry of palladium complexes of the phenyl diazaphospholes,[11] the nitrogen substituents were observed to have a dominant effect on the stereochemical outcome of the reactions studied. For example, the addition of diazaphosphole oxide **4e** [R = $(CH_3)_3CH_2$] to aldehydes proceeded with higher diastereoselectivity and with the opposite induced stereochemistry when compared to the diazaphospholes **4a** [R = $PhCH_2$]. It was proposed that the conformation adopted by the nitrogen substituents was a critical factor in determining the stereochemical outcome of the reaction. The oxides **4c**, **4e** and **4i** and the phenyl diazaphosphole **3e**[11] gave crystals suitable for structural analysis using X-ray diffraction, and therefore allowed a thorough investigation of the conformations adopted by the nitrogen substituents (in solid).

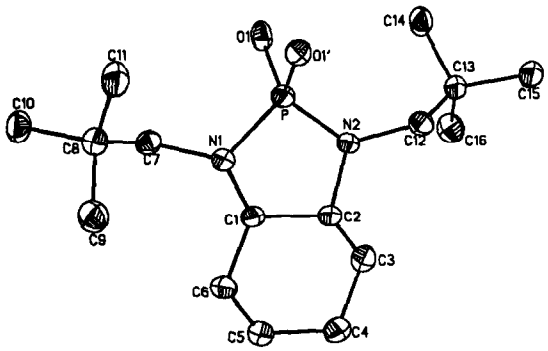


Figure 2 (above) The molecular structure of diazaphosphole oxide **4e** shown with 50% probability displacement ellipsoids (peripheral H atoms have been omitted for clarity).

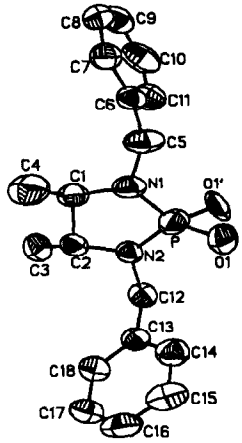


Figure 3 (above). The molecular structure of diazaphosphole oxide **4i** shown with 50% probability displacement ellipsoids.

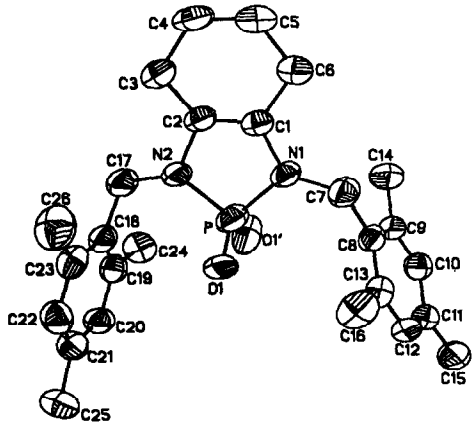


Figure 4. The molecular structure of diazaphosphole oxide **4c** shown with 50% probability displacement ellipsoids.

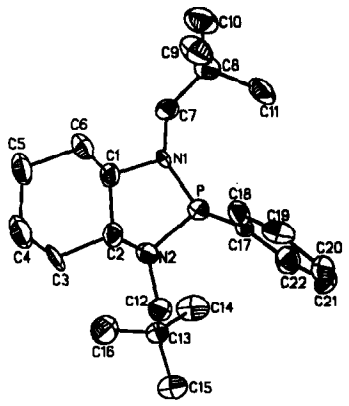


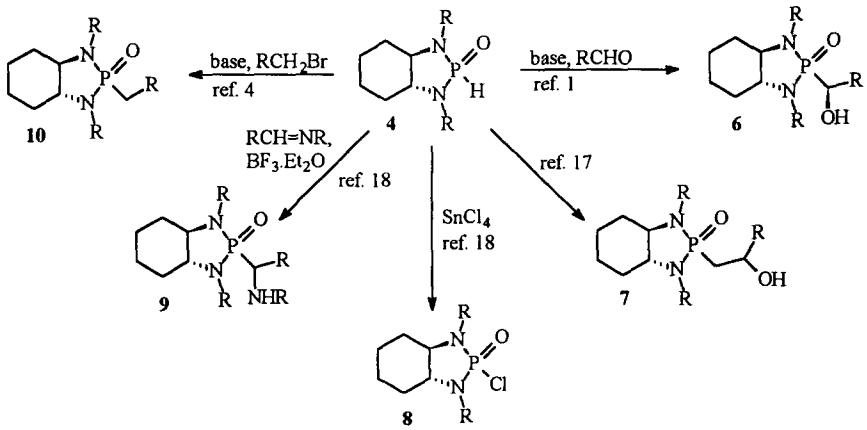
Figure 5. The molecular structure of phenyl-diazaphosphole **3e** shown with 75% probability displacement ellipsoids.

In the 1,2-additions of diazaphosphole oxides **4** to cinnamaldehyde,[1] the N-neopentyl system **4e** gave 78% d.e., the monocyclic system **4i** gave 33% d.e., and the N-mesityl system **4c** gave 13% d.e. The structures (Figures 2-5) clearly show that the substituents on nitrogen (R^1) and the substituents at the chiral centers (R^2) have substantial effects on the preferred conformation of the overall molecule. The crystal lattice of all three diazaphosphole oxides have a disordered oxygen atom, which led to structural refinement with two positions for the oxygen atom attached to phosphorus (Figures 2-4). All measured bond lengths were in agreement with the expected values for N-C, P-N, and C-C sp^3-sp^3 bonds.[12]

The conformation and bond angles in the N-neopentyl diazaphosphole oxide **4e** closely resemble the structures of previously reported N-neopentyl[11,14] and N-methyl[15] phosphonamides (2-alkyl diazaphosphole oxides). The fused six membered ring clearly distorts the phosphorus containing five membered ring in comparison to **4i** and related monocyclic phosphonamides.[16] In the monocyclic system **4i**, the phenyl rings lie "anti" to each other in spite of the fact that the nitrogen atoms are nearly planar, and are also positioned well above and below the plane of the five-membered ring. In **4c**, the mesityl groups are "eclipsed" and they lie in nearly the same plane of the five-membered ring. Finally, the *tert*-butyl groups of the neopentyl system **4e** are anti to one another, but on opposite sides of the plane from their adjacent N-methylene carbons.

The geometries at the nitrogen atoms of the three diazaphosphole oxides are distinctly different. The sums of the nitrogen bond angles (ΣN) indicate that the geometry of nitrogen is nearly planar for the monocyclic system **4i** [ΣN(1) = 357.5(6), ΣN(2) = 354.8(6)], midway between planar and tetrahedral for the neopentyl system **4e**, [ΣN(1) = 344.5(9), ΣN(2) = 343.6(9)], and intermediate for mesityl system **4c**. [ΣN(1) = 346.8(6), ΣN(2) = 351.4]. As a result, the N-methylene substituents in each diazaphosphole oxide were anti to one another, but to differing degrees. The extent of these variations was determined by calculating a mean plane of the five-membered ring and measuring the out-of-plane distances of the N-methylene carbons. The differences in these out-of-plane distances was inversely proportional to the sums of the nitrogen bond angles: **4e** > **4c** > **4i**. Out-of-plane distortions can also be considered from the perspective of a N-N line. A comparison of the angles between the N-N line and the bond to the N-methylene carbon led to the same conclusion as the measurement of out-of-plane distances: 30.4 and 30.8° in the neopentyl system **4e**, 25.5 and 22.6° in the mesityl system **4c**, and 16.7 and 19.2° in the monocyclic system **4i**.

Scheme 2



It has been shown that diazaphosphole oxides **4** are excellent nucleophilic phosphonylating reagents (Scheme 2) for alkyl halides, epoxides, aldehydes and imines, and that they can be oxidized to the chlorides under mild conditions. The products of these reactions, the phosphonamides **6** and **10**, and chlorides **8**, also have applications in asymmetric chemistry.[6,19] The structural data presented in this paper should aid in the refinement of diazaphospholes for future applications in asymmetric synthesis.

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Experimental

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-300 spectrometer at 300, 75 and 121 MHz, respectively. The ^1H chemical shifts are reported in ppm downfield from Me_4Si. The ^{31}P chemical shifts are reported in ppm relative to external H_3PO_4. The ^{13}C chemical shifts are reported in ppm relative to the center line of C_6D_6 (128.0 ppm) or the center line of $CDCl_3$ (77.0 ppm). Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Optical rotations were determined on a Rudolf Research Autopol III polarimeter. Mass spectra were determined on a Varian Mat 331A spectrometer, and microanalyses were performed by Atlantic Microlab Inc. High resolution mass spectra were performed by Monsanto Company. Toluene and CH_2Cl_2 were distilled from CaH_2, and THF and Et_2O were distilled from sodium-benzophenone ketyl. Et_3N was distilled twice from KOH.

X-ray structure determinations were performed on a Siemens R3 automated single crystal x-ray diffractometer using a graphite monochromated Mo Kα radiation. Data reduction and structure solution were carried out using XDISK.[20] Structure solution and least-squares refinement for all compounds were achieved by using SHELXTL.[20] Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$. The non-hydrogen atoms were treated using an appropriate riding model (AFIX m3, SHELXTL). Crystal and intensity data, collection parameters, the final residual values, the relevant structure refinement parameters, the atomic coordinates for the non-hydrogen atoms, the positional and isotropic displacement coefficients for hydrogen atoms, a list of anisotropic displacement coefficients for the non-hydrogen atoms, the calculated and observed structure factors, and a complete list of bond distances and bond angles have been deposited with the Cambridge Crystallographic Data Base

(*1R,2R*)-N,N'-dibenzyl-1,2-cyclohexanediamine (1a). To suspension of (*R,R*)-1,2-cyclohexanediamonium-(+)-tartrate (20 g, 100 mmol) in MeOH (60 mL) was added a solution of potassium hydroxide (11.2 g, 200 mmol) in MeOH (80 mL) over a period of 1 hour. When the addition was complete, the mixture was stirred for 30 minutes and then filtered. The filtrate was concentrated *in vacuo* and redissolved in MeOH (160 mL) and benzaldehyde (21.39 mL, 210 mmol) was added *via* syringe. The reaction mixture was heated to reflux for 1 hour. The solution was allowed to cool to room temperature, then was cooled further to 0 °C, and sodium

borohydride (11.3 g, 300 mmol) was added. The mixture was stirred at room temperature overnight, and it was then poured into ice water (400 mL). After the ice melted, KOH (2 g) was added and the product was extracted with CH_2Cl_2 (5x100 mL). The extracts were combined, dried (Na_2SO_4), and concentrated *in vacuo* to give a colorless oil (21.1 g), which contained product and benzyl alcohol. The oil was dissolved in MeOH (100 mL) and a solution of conc. HCl (16.0 mL, 194 mmol) in MeOH (100 mL) was added slowly. The mixture was concentrated *in vacuo* to give an off-white solid, which was recrystallized from MeOH/Et_2O to give a white crystalline solid (22.7g, 62%). mp (2HCl salt) 241-244 °C; $[\alpha]_D$ = -61.6°(2HCl salt, *c* = 1.03, H_2O); IR (KBr/2HCl salt) 2945, 2760 (brd) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (m, 10 H), 3.66 (ABq, 4 H, $\Delta\nu_{AB}$ = 62.0 Hz, J_{AB} = 13.4 Hz), 2.24 (m, 2 H), 1.96 (m, 2 H), 1.51 (m, 2 H), 1.04 (m, 2 H), 0.91 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 141.1, 128.3, 128.1, 126.7, 60.9, 50.9, 31.6, 25.1; MS(EI/DIP) m/z (rel. intensity) 294 (M^+, 93), 203 (100), 189 (93). Anal. Calcd for $C_{20}H_{28}N_2Cl_2$: C, 65.39; H, 7.68; N, 7.63. Found: C, 65.29; H, 7.69; N, 7.65.

(*1R,2R*)-N,N'-Bis-[(2-methylphenyl)-methyl]-1,2-diaminocyclohexane (1b). Prepared according to procedure for **3a**. mp (2HCl salt) 211-213 °C (MeOH/Et_2O); $[\alpha]_D$ = -71.2 (2HCl salt, *c* = 1.02, H_2O); IR (KBr/2HCl salt) 3425 (brd), 2945, 2745 (brd), 2365 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 2 H), 7.12 (m, 6 H), 3.73 (ABq, 4 H, $\Delta\nu_{AB}$ = 80.3 Hz, J_{AB} = 12.9 Hz), 2.30 (s, 6 H), 2.24 (m, 2 H), 1.74 (br s, 4 H), 1.34-1.20 (m, 2 H), 1.00-1.12 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 138.7, 136.2, 130.0, 128.3, 126.9, 125.7, 61.4, 48.9, 31.7, 25.1, 19.0; MS(EI/DIP) m/z (rel. intensity) 322 (M^+, 17), 217 (29), 105 (100), 104. Anal. Calcd for $C_{22}H_{32}N_2Cl_2$: C, 66.83; H, 8.16; N, 7.08. Found: C, 66.79; H, 8.20; N, 7.13.

(*1R,2R*)-N,N'-Bis[(1-naphthyl)-methyl]-1,2-diaminocyclohexane (1d). Prepared according to the procedure for **3a**, (39%). mp (2HCl salt) 227-230.5 °C (EtOH/Et_2O); $[\alpha]_D$ = -99.0 (*c* = 1.0, 95% EtOH); IR (KBr/2HCl salt) 3425 (brd), 2940, 2720(brd), 2365, cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 (m, 2 H), 7.80-7.69 (m, 4 H), 7.42-7.19 (m, 8 H), 4.17 (AB, 4 H, $\Delta\nu_{AB}$ = 86.1 Hz, J_{AB} = 13.0 Hz), 2.42-2.29 (m, 4 H), 1.79 (m, 2 H), 1.40-1.10 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 133.6, 133.5, 131.2, 128.5, 128.1, 126.3, 126.2, 125.5, 125.0, 123.0, 60.4, 47.7, 30.3, 24.7; MS(EI/DIP) m/z (rel. intensity) 253 (37), 157 (40), 156 (37), 141 (100),. Anal. Calcd for $C_{28}H_{32}N_2Cl_2$: C, 71.94; H, 6.90; N, 5.99. Found: C, 71.79; H, 6.97; N, 5.92.

(*1R,2R*)-N,N'-Bis(2,2-dimethylpropyl)-1,2-cyclohexanediamine (1e). Prepared according to the procedure for **3a** (83%). mp(2HCl salt) 261-263 °C; $[\alpha]_D$ = -57.9 (2HCl salt, *c* = 1.01, H_2O); IR ($CHCl_3$) 3315 (brd), 2950 (brd) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.55 (d, 2 H, J = 11.0 Hz), 2.10 (d, 2 H, J = 11.2 Hz), 2.10 (m, 2 H), 2.02 (m, 2 H), 1.69 (m, 2 H), 1.50 (s, 2 H), 1.20 (m, 2 H), 0.98 (m, 2 H), 0.90 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 63.2, 59.9, 32.1, 31.7, 27.9, 25.3; MS(EI/DIP) m/z (rel. intensity) 197 (100), 112 (67). Anal. Calcd for $C_{16}H_{36}N_2Cl_2$: C, 58.70; H, 11.08; N, 8.56. Found: C, 58.65; H, 11.14; N, 8.57.

(*1R,2R*)-N,N'-Bis-(3-methylbutyl)-1,2-diaminocylohexane (1f). Prepared according to the procedure for **3a**, (60%). mp(2HCl salt) 241.0-243.0 °C (EtOH/Et_2O); $[\alpha]_D$ = -55.7 (2HCl salt, *c* = 0.95, H_2O); IR ($CHCl_3$) 3415 (brd), 3020, 2930, 2400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.79-2.68 (m, 2 H), 2.47-2.36 (m, 2 H), 2.14-2.02 (m, 4 H), 1.75-1.55 (m, 4 H), 1.50-1.40 (m, 1 H), 1.40-1.28 (m, 4 H), 1.28-1.15 (m, 3 H), 1.05-0.90 (m, 2 H), 0.89 (d, 12 H, J = 6.7 Hz); ^{13}C NMR (CDCl) δ 62.0, 45.1, 39.7, 31.8, 26.1, 25.2, 22.8, 22.6; MS(CI/GC/CH) m/z

(rel. intensity) 255 ([M+1]$^+$, 100), 253 (84), 197 (62), 168 (91). Anal. Calcd for $C_{16}H_{36}N_2Cl_2 \cdot 0.5H_2O$: C, 57.13; H, 11.09; N, 8.33. Found: C, 57.00; H, 11.06; N, 8.33.

(±)-N,N'-Bis[(2,4,6-trimethylphenyl)-methyl]-1,2-diaminocyclohexane (1c). To a solution of mesitylaldehyde (2.50 mL, 17.0 mmol) in toluene (25 mL) cooled to 0 °C was added (±)-*trans*-1,2-diaminocyclohexane (0.969 mL, 8.1 mmol) *via* syringe. The ice bath was removed and the reaction mixture was heated to reflux for 1 hr. The mixture was then concentrated by distilling off toluene (20 mL). After cooling to room temperature, methanol (15 mL) was added and the mixture was cooled to 0 °C. Sodium borohydride (0.916g, 24.2 mmol) was added and the ice bath was removed. After 2 h, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (4x50 mL). The extracts were combined, dried (Na_2SO_4), and concentrated *in vacuo* to give a white solid. The solid was triturated with diethyl ether to give a white crystalline solid (2.3 g, 74%). mp 139-140 °C; IR (KBr) 3425 (brd), 3290, 2925, 2855, 1660 cm^{-1}: ^{1}H NMR ($CDCl_3$) δ 6.80 (s, 4 H), 3.63 (AB, 4 H, $\Delta\nu_{AB}$ = 111.5 Hz, J_{AB} = 11.2 Hz), 2.35 (s, 2 H), 2.28 (s, 12 H), 2.24 (s, 6 H), 2.18 (m, 2 H), 1.78 (m, 2 H), 1.50 (s, 2 H), 1.30 (m, 2 H), 1.08 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 136.7, 136.0, 134.0, 128.7, 62.0, 45.1, 32.0, 25.2, 21.0, 19.6; MS(EI/DIP) m/z (rel. intensity) 133 (100), 132 (29). Anal. Calcd for $C_{26}H_{38}N_2$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.28; H, 10.15; N, 7.32.

***(1R,2R)*-N,N'-Bis(2-propyl)-1,2-cyclohexanediamine (1g).** (*R,R*)-1,2-cyclohexanediamonium-(+)-tartrate (10.01g, 50.0 mmol) and H_2O (10 mL) were added and a solution of NaOH (4.00g, 100 mmol) in H_2O (25 mL) was added (to the resulting suspension) via addition funnel over a period of 30 min. After the addition was complete, toluene (60 mL), sodium bicarbonate (15.12 g, 180 mmol), and lastly isopropyl iodide (14.96 mL, 150 mmol) were added, each in one portion. The addition funnel was replaced with a reflux condenser and the reaction mixture was heated to reflux for 1 hour. Upon cooling, the mixture was diluted with toluene (100 mL) and the aqueous layer was discarded. The toluene solution was washed with water (7x50 mL), dried (Na_2SO_4), and concentrated *in vacuo* to give a yellow oil (4.8g). This oil was vacuum distilled to give a colorless oil (3.6g, 36%). Bp 54 °C at 10 millitorr; $[\alpha]_D$ = -82.3 (2HCl salt, *c* = 0.99, H_2O); IR ($CHCl_3$) 3300, 2925 (brd) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.87 (m, 2 H), 2.13 (m, 2 H), 2.08 (m, 1 H), 2.03 (m, 1 H), 1.68 (m, 2 H), 1.23 (m, 4 H), 1.05 (d, 6 H, J = 6.4 Hz), 0.99 (d, 6 H, J = 6.1 Hz), 0.95 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 59.1, 45.5, 32.6, 25.1, 22.7; MS(EI/DIP) m/z (rel. intensity) 91 (100). Anal. Calcd for $C_{12}H_{26}N_2$: C, 72.66; H, 13.21; N, 14.12. Found: C, 72.52; H, 13.19; N, 14.07.

General Procedure for Phosphorous Acid Diamides (Diazaphosphole oxides) (4). To a solution of PCl_3 (3.85 mmol) and Et_3N (7.70 mmol) in toluene (12 mL) at -60 °C was added and a solution of the diamine **1** (3.50 mmol) in toluene (12 mL) over 30 min. The cooling bath was removed, and after 2 h. the mixture was filtered through $MgSO_4$. The solution was again cooled to -60 °C and Et_3N (3.85 mmol) and water (3.50 mmol) were added. The cooling bath was removed, and after 1 h. the mixture was filtered through $MgSO_4$. The solvent was removed *in vacuo* using a mechanical pump to yield the crude product. Crude and isolated yields and method of isolation for each compound are given below. NMR spectra were recorded in C_6D_6 solution (unless otherwise indicated).

(*3aR,7aR*)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-dibenzyl-1*H*-1,3,2-benzodiazaphosphole-2-oxide (4a). Trituration from Et_2O (80%). mp 129-131 °C; $[\alpha]_D$ = -55.5 (*c* = 1.0, $CHCl_3$); IR (KBr) 2940, 2310, 1450, 1220cm^{-1}; ^{1}H NMR δ 7.54 (d, 1 H, J_{PH} = 591.7 Hz), 7.25 (m, 10 H), 4.23 (dd, 1 H, J_{PH} = J_{HH} = 15.6 Hz), 4.08 (dd, 1 H, J_{PH} = J_{HH} = 15.6 Hz), 3.97 (dd, 1 H, J = 15.4, 10.5 Hz), 3.72 (dd, 1 H, J = 15.9, 7.4 Hz), 2.72 (m, 1 H), 2.46 (m, 1 H), 1.48 (m, 2 H), 1.19 (s, 2 H), 0.70 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 138.2, 138.0, 128.4, 128.3, 128.0, 127.8, 127.2, 127.1, 63.1 (d, $^2J_{PC}$ = 8.5 Hz), 62.8 (d, $^2J_{PC}$ = 5.7 Hz), 46.6 (d, $^2J_{PC}$ = 3.2 Hz), 46.0 (d, $^2J_{PC}$ = 6.4 Hz), 29.4 (d, $^3J_{PC}$ = 7.9 Hz), 28.7(d, $^3J_{PC}$ = 7.9 Hz), 24.2, 24.1; ^{31}P NMR δ 19.9; MS(CI/GC/CH_4) m/z (rel. intensity) 355 $(M+Me)^+$, 297 (32), 281 (100). Anal. Calcd for $C_{20}H_{25}N_2OP$: C, 70.57; H, 7.40; N, 8.23. Found: C, 70.34; H, 7.47; N, 8.18.

(*3aR,7aR*)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-bis-[(2-methylphenyl)-methyl]-1*H*-1,3,2-benzodiazaphosphole-2-oxide (4b). (Crude yield 85%), Column chromatography (SiO_2 eluting with 99:1 $CHCl_3$/MeOH), (57%). Oil, $[\alpha]_D$ = -57.2 (*c* = 0.94, $CHCl_3$); IR ($CHCl_3$) 3025, 2935, 2250, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.48 (m, 1 H), 7.39 (m, 1 H), 7.32 (d, 1 H, J_{PH} = 605.8 Hz), 7.25-7.10 (m, 6 H), 4.43 (dd, 1 H, J = 15.6, 11.6 Hz), 4.27 (dd, 1 H, J = 15.7, 13.4 Hz), 4.14 (dd, 1 H, J = 16.1, 9.3 Hz), 3.93 (dd, 1 H, J = 15.4, 13.0 Hz), 3.15-3.05 (m, 1 H), 3.00-2.90 (m, 1 H), 2.34 (s, 3 H), 2.34 (s, 3 H), 1.90-1.65 (m, 4 H), 1.10-1.30 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 136.2 (d, $^3J_{PC}$ = 4.4 Hz), 136.0 (d, $^3J_{PC}$ = 4.4 Hz), 135.8, 135.5, 130.2, 130.0, 128.4, 127.8, 127.1, 127.0, 125.9, 125.7, 64.5 (d, $^2J_{PC}$ = 5.2 Hz), 64.0 (d, $^2J_{PC}$ = 6.3 Hz), 44.7 (d, $^2J_{PC}$ = 2.9 Hz), 44.2 (d, $^2J_{PC}$ = 6.6 Hz), 29.6 (d, $^3J_{PC}$ = 10.0 Hz), 28.9 (d, $^3J_{PC}$ = 7.2 Hz), 24.3, 24.2, 19.4, 19.3; ^{31}P NMR ($CDCl_3$) δ 22.3; MS(EI/DIP) m/z (rel. intensity) 217 (20), 105 (100), 104 (25). Anal. Calcd for $C_{22}H_{29}N_2OP{\cdot}H_2O$: C, 68.37; H, 8.08; N, 7.25. Found: C, 68.62; H, 7.75; N, 7.27.

(±)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-bis-[(2,4,6-trimethylphenyl)-methyl]-1*H*-1,3,2-benzodiazaphosphole-2-oxide (4c). Recrystallization from EtOAc (62%). mp 173-178 °C; IR (KBr) 2925, 2855, 2350, 1235 cm^{-1}; ^{1}H NMR δ 6.79 (d, 1 H, J_{PH} = 597.0 Hz), 6.74 (s, 2 H), 6.66 (s, 2 H), 4.08 (dd, 1 H, J = 12.5, 5.7 Hz), 3.81 (dd, 1 H, J_{HH} = J_{PH} = 10.7 Hz), 3.70 (dd, 1 H, J = 12.7, 7.6 Hz), 3.60 (dd, 1 H, J_{HH} = J_{PH} = 10.9 Hz), 2.83-2.75 (m, 1 H), 2.59-2.50 (m, 1 H), 2.48 (s, 6 H), 2.32 (s, 6 H), 2.08 (s, 3 H), 2.03 (s, 3 H), 1.74-1.59 (m, 2 H), 1.40 (br s, 2 H), 1.20-0.85 (m, 4 H); ^{13}C NMR δ 138.3, 137.8, 137.3, 137.0, 129.5, 128.3, 127.7, 66.0, 64.0, 43.1, 42.2, 29.7, 29.0, 24.7, 21.2, 20.7; ^{31}P NMR δ 17.7; MS(EI/DIP) m/z (rel. intensity) 133 (100), 132 (21). Anal. Calcd for $C_{26}H_{37}N_2OP{\cdot}0.5H_2O$: C, 72.03; H, 8.83; N, 6.46. Found: C, 72.31; H, 8.74; N, 6.50.

(*3aR,7aR*)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-bis-[(1-naphthyl)-methyl]-1*H*-1,3,2-benzodiazaphosphole-2-oxide (4d). Column chromatography (SiO_2 eluting with 99:1 $CHCl_3$/MeOH), (52%). Waxy solid; $[\alpha]_D$ = -50.2 (*c* = 1.48, $CHCl_3$); IR (KBr) 2935, 2365, 1635, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.10 (m, 1 H), 7.87-7.63 (m, 4 H), 7.61-7.37 (m, 5 H), 7.35 (d, 1 H, J_{PH} = 607.9 Hz), 7.28-7.08 (m, 4 H), 4.89 (dd, 1 H, J = 15.8, 11.4 Hz), 4.76 (dd, 1 H, J_{HH} = J_{PH} = 16.1 Hz), 4.59 (dd, 1 H, J = 16.1, 8.3 Hz), 4.46 (dd, 1 H, J = 15.3, 13.7 Hz), 3.27-3.18 (m, 1 H), 3.10-3.02 (m, 1 H), 1.93 (br s, 1 H), 1.78 (br s, 1 H), 1.70-1.60 (m, 2 H), 1.30-1.10 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 133.6, 133.5, 131.2, 131.0, 128.7, 128.6, 128.0, 127.9, 126.3, 126.2, 126.0, 125.7, 125.6, 125.5, 125.3, 125.2, 123.04, 123.00, 64.9 (d, $^2J_{PC}$ = 5.2 Hz), 64.1 (d, $^2J_{PC}$ = 7.8 Hz), 44.7 (d, $^2J_{PC}$ = 3.0 Hz), 44.2 (d, $^2J_{PC}$ = 6.9 Hz), 29.6 (d, $^3J_{PC}$ = 9.9 Hz), 29.0 (d, $^3J_{PC}$ = 7.3 Hz), 24.3, 24.2; ^{31}P NMR ($CDCl_3$) δ 22.7;

MS(CI/DIP/CH_4) m/z (rel. intensity) 741 (38), 601 (100), 567 (35), 301 (42), 283 (34). HRMS(CI/CH_4), $(M+1)^+$ calcd for $C_{28}H_{33}N_2OP$: 441.2096. Found: 441.2148.

(*3aR,7aR*)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-bis(2,2-dimethylpropyl)-1*H*-1,3,2-benzodiazaphosphole-2-oxide (4e). Trituration from hexanes (90%). mp 100-102 °C; $[\alpha]_D$ = -103.6 (*c* = 1.0, $CHCl_3$); IR (KBr) 2950, 2870, 2335, 1235 cm^{-1}; ^1H NMR δ 7.31 (d, 1 H, J_{PH} = 587.3 Hz), 3.57 (dd, 1 H, J = 15.3, 14.2 Hz), 2.63 (dd, 1 H, J = 17.8, 14.5 Hz), 2.51 (m, 1 H), 2.29 (m, 1 H), 2.26 (dd, 1 H, J_{HP} = J_{HH} = 14.5 Hz), 1.96 (dd, 1 H, J_{HP} = J_{HH} = 14.4 Hz), 1.56 (m, 2 H), 1.40 (m, 2 H), 1.14 (m, 2 H), 0.97 (s, 9 H), 0.91 (s, 9 H), 0.85 (m, 2 H); ^{13}C NMR δ 65.5, 64.1, 64.0, 55.8, 55.0, 32.6, 31.2, 30.2, 28.5, 28.1, 24.6, 24.5; ^{31}P NMR δ 32.9; MS(EI/DIP) m/z (rel. intensity) 243 (100), 197 (99), 112 (63). Anal. Calcd for $C_{16}H_{33}N_2OP$: C, 63.97; H, 11.07; N, 9.32. Found: C, 63.79; H, 11.10; N, 9.41.

(*3aR,7aR*)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-bis(3-methylbutyl)-1*H*-1,3,2-benzodiazaphosphole-2-oxide (4f). Column chromatography (SiO_2 eluting with 99:1 $CHCl_3$/MeOH), (63%). Oil, $[\alpha]_D$ = -72.0 (*c* = 0.56, $CHCl_3$); IR ($CHCl_3$) 2955, 2870, 2350, 2255 1210 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (d, 1 H, J_{PH} = 592.9 Hz), 3.20-2.65 (m, 6 H), 2.05-1.94 (m, 2 H), 1.88-1.76 (m, 2 H), 1.68-1.53 (m, 2 H), 1.53-1.36 (m, 4 H), 1.35-1.24 (m, 3 H), 1.19-1.09 (m, 1 H), 0.90 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 62.7 (d, $^2J_{PC}$ = 5.5 Hz), 62.3 (d, $^2J_{PC}$ = 8.2 Hz), 40.9 (d, $^2J_{PC}$ = 2.2 Hz), 40.4 (d, $^2J_{PC}$ = 5.6 Hz), 38.5 (d, $^4J_{PC}$ = 2.0 Hz), 37.8 (d, $^4J_{PC}$ = 2.1 Hz), 29.3 (d, $^3J_{PC}$ = 10.3 Hz), 28.4 (d, $^3J_{PC}$ = 7.8 Hz), 26.1, 24.2 (d, $^3J_{PC}$ = 6.7 Hz), 22.7, 22.6, 22.5, 22.4; ^{31}P NMR ($CDCl_3$) δ 21.5; MS(CI/DIP/CH_4) m/z (rel. intensity) 301 ($[M+1]^+$ (100), 298. HRMS(CI/CH_4), $(M+1)^+$ calcd for $C_{16}H_{33}N_2OP$: 301.2409. Found: 301.2423.

(3aR,7aR)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-bis(2-propyl)-1*H*-1,3,2-benzodiazaphosphole-2-oxide (4g). Column chromatography (SiO_2 eluting with 99:1 $CHCl_3$/MeOH), (54%). Liquid, $[\alpha]_D$ = -133.4.(c = 0.95, $CHCl_3$); IR (KBr) 2935, 2340, 1210 cm^{-1}; ^1H NMR δ 7.67 (d, 1 H, J_{PH} = 578.2 Hz), 3.17 (m, 2 H), 2.90 (m, 1 H), 2.50 (m, 1 H), 1.62 (m, 2 H), 1.45 (d, 3 H, J = 6.9 Hz), 1.43 (m, 2 H), 1.30 (d, 3 H, J = 7.0 Hz), 1.24 (d, 3 H, J = 6.5 Hz), 0.97 (d, 3 H, J = 6.6 Hz), 0.94 (m, 2 H), 0.75 (m, 2 H); ^{13}C NMR δ 61.2, 59.9, 45.3, 44.6, 29.2, 24.5, 22.9, 21.2; ^{31}P NMR δ 10.4; MS(CI/DIP/CH_4) m/z (rel. intensity) 245 ($[M+1]^+$ 1(00), 229 (77)). HRMS(CI/CH_4), $(M+1)^+$ calcd for $C_{12}H_{25}N_2OP$: 245.1783. Found: 245.1784.

(±)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-diphenyl-1*H*-1,3,2-benzodiazaphosphole-2-oxide (4h). (Crude yield 95%) not isolated. Waxy solid, IR (KBr) 3035, 2945, 2865, 2385, 2250, 1600, 1250 cm^{-1}; ^1H NMR δ 7.52 (d, 1 H, J_{PH} = 618.4 Hz), 7.36 (d, 2 H, J = 8.5 Hz), 7.25-7.05 (m, 5 H), 7.00-6.90 (m, 2 H), 6.77 (m, 1 H), 3.40 (m, 1 H), 3.13 (m, 1 H), 2.18 (m, 1 H), 1.99 (m, 1 H), 1.79 (m, 1 H), 1.32 (m, 2 H), 1.00-0.80 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 138.9 (d, $^2J_{PC}$ = 5.6 Hz), 138.6 (d, $^2J_{PC}$ = 1.9 Hz), 129.3, 125.3, 125.2, 125.01, 124.96, 124.41, 124.39, 122.14, 122.09, 62.5 (d, $^2J_{PC}$ = 7.3 Hz), 62.4 (d, $^2J_{PC}$ = 6.6 Hz), 28.9 (d, $^3J_{PC}$ = 8.4 Hz), 28.1 (d, $^3J_{PC}$ = 6.0 Hz), 24.22, 24.16; ^{31}P NMR δ 13.3; MS(CI/DIP/CH_4) m/z (rel. intensity) 313 ($[M+1]^+$ (39), 267 (88), 266 (57), 245 (82), 174 (100). HRMS(CI/CH_4), $(M+1)^+$ calcd for $C_{18}H_{21}N_2OP$: 313.1470. Found: 313.1474.

(±)-2,3,4,5-Tetrahydro-1,3-dibenzyl-4,5-dimethyl-1*H*-1,3,2-diazaphosphole-2-oxide (4i). Trituration from Et_2O (62%). mp 108.5-110 °C; IR (KBr) 3100 (brd), 2970, 2345 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.62 (d, 1 H, J_{PH} = 606.0 Hz), 7.46 (m, 2 H), 7.38-7.23 (m, 8 H), 4.39 (dd, 2 H, J = 15.9, 9.2 Hz), 4.33 (dd, 2 H, J = 15.1, 10.2 Hz), 4.12 (two overlaping dd, 2 H, J_{obs} = 14.9, 11.9, 7.8 Hz), 2.99-2.84 (m, 2 H), 1.08 (d, 3 H, J = 6.1 Hz), 1.02 (d, 3 H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ 137.5, 128.6, 127.9, 127.4, 58.3 (d, $^2J_{PC}$ = 8.0 Hz), 57.5 (d, $^2J_{PC}$ = 9.0 Hz), 46.0 (d, $^2J_{PC}$ = 3.2 Hz), 45.4 (d, $^2J_{PC}$ = 6.0 Hz), 18.4, 17.8; ^{31}P NMR δ 14.8; MS(EI/DIP) m/z (rel. intensity) 314 (60), 134 (76), 91 (100). Anal. Calcd for $C_{18}H_{23}N_2OP$: C, 68.77; H, 7.37; N, 8.91. Found: C, 68.57; H, 7.42; N, 8.85.

(±)-Tetrahydro-1,3-dibenzyl-4,5-diphenyl-2,3,4,5-1*H*-1,3,2-diazaphosphole-2-oxide (4j). (97%). mp 134.5-136 °C (EtOAc/hexanes); IR (KBr) 3060, 3025, 2930, 2870, 2400, 1600, 1210 cm^{-1}; ^1H NMR δ 9.00 (S, 0.5 H), 7.09 (m, 20.5 H), 4.37-4.26 (m, 2 H), 4.07 (m, 1 H), 3.99 (dd, 1 H, J = 8.0, 4.9 Hz), 3.66-3.52 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 139.4, 138.2, 136.3, 128.9, 128.7, 128.4, 128.2, 128.1, 127.4, 127.1, 68.2, 67.8, 67.7, 46.4, 45.8; ^{31}P NMR δ 15.1; MS(EI/DIP) m/z (rel. intensity) 438 (M^{+}) (15), 347 (52), 196 (34), 91 (100). Anal. Calcd for $C_{28}H_{27}N_2OP$: C, 76.69; H, 6.21; N, 6.39. Found: C, 76.47; H, 6.27; N, 6.34.

General Procedure for Thiophosphorous Acid Diamides (Diazaphosphole sulfides) (5). To a solution of PCl_3 (3.85 mmol) and Et_3N (7.70 mmol) in toluene (12 mL) cooled to -60 °C was added a solution of the diamine **1** (3.50 mmol) in toluene (12 mL) over 30 min. The cooling bath was removed, and after 2 h. the mixture was filtered through $MgSO_4$. The solution was again cooled to -60 °C and Et_3N (3.85 mmol) was added. H_2S gas was bubbled into the solution until the precipitation of triethylamine hydrochloride had ceased. The cooling bath was removed, and after 1 h. the mixture was filtered through $MgSO_4$. The solvent was removed *in vacuo* using a mechanical pump to yield the crude product. Crude and isolated yields and method of isolation for each compound are given below.

(*3aR,7aR*)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-dibenzyl-1*H*-1,3,2-benzodiazaphosphole-2-sulfide (5a). column chromatography (SiO_2 eluting with 1:1 EtOAc/hexanes) (40%); mp 122-123.5 °C; ^1H NMR ($CDCl_3$) δ 7.54 (d, 1 H, J_{PH} = 591.7 Hz), 7.25 (m, 10 H), 4.23 (dd, 1 H, J_{HH} = J_{HP} = 15.6 Hz), 4.08 (dd, 1 H, J_{HH} = J_{HP} = 15.6 Hz), 3.97 (dd, 1 H, J = 15.4, 10.5 Hz), 3.72 (dd, 1 H, J = 15.9, 7.4 Hz), 2.72 (m, 1 H), 2.46 (m, 1 H), 1.48 (m, 2 H), 1.19 (s, 2 H), 0.70 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 128.7, 128.6, 127.4, 63.1, 62.8, 46.9, 46.4, 29.4, 29.3, 24.3; ^{31}P NMR ($CDCl_3$) δ 62.6.

(*3aR,7aR*)-2,3,3a,4,5,6,7,7a-Octahydro-1,3-bis(2,2-dimethyl-propyl)-1*H*-1,3,2-benzodiazaphosphole-2-sulfide (5b). Column chromatography (SiO_2 eluting with 1:1 EtOAc/ hexanes) (67%). mp 93.5-94.5 °C; $[\alpha]_D$ = -110. (*c* = 1.0 , $CHCl_3$); IR (KBr) 2962, 2332 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.32 (d, 1 H, J_{PH} = 585 Hz), 3.52 (dd, 1 H, J_{HH} = J_{HP} = 14.4 Hz), 3.22 (dd, 1 H, J = 11.0, 11.1 Hz), 3.07 (m, 1 H), 2.85 (dd, 1 H, J = 15.3, 15.1 Hz) 2.54 (m, 1 H), 2.32 (dd, 1 H, J = 14.4 and 14.3 Hz), 2.18 (m, 2 H), 1.99 (m, 2 H), 1.84 (m, 2 H), 1.25 (m, 1H), 0.97 (s, 9 H), 0.91 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 66.2, 64.1, 55.2, 53.0, 34.9, 32.5, 31.1, 30.9, 29.2, 29.0, 28.6, 24.6; ^{31}P NMR ($CDCl_3$) δ 70.7; Anal. Calcd for $C_{16}H_{33}N_2PS$: C, 60.72; H, 10.51; N, 8.85. Found: C, 60.54; H, 10.55; N, 8.81.

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