Synthesis and Aza-Wittig Reactions of Cyclic Amino Phosphonium Salts

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Cyclic phosphonium salts are versatile reagents for the synthesis of unsymetrical unconjugated dienes,[1,2] because their Wittig reactions provide alkenylphosphine oxides which can be subjected to further alkenation by the Horner–Wittig reaction. Applications of these tandem Wittig reactions include syntheses of insect sex pheromones,[3] 1,4-diketones,[4] cycloheptenyldiphenylphosphine oxide derivatives[5,6] and hydroazulenes.[6]

The aza-Wittig reactions of aza-ylides have also received much attention and have been applied to the synthesis of C=N bond-possessing compounds, especially nitrogen heterocycles.[7] Although numerous articles have appeared on the reactions and synthetic applications of acyclic aza-ylides,[8] the preparations of cyclic aza-ylides are less explored.[9]

In our continuing studies on the application of cyclic phosphonium salts to organic synthesis, we would like to describe a synthesis and some aza-Wittig reactions of cyclic 2-amino phosphonium salts (Figure 1) and their aza-Wittig reactions with simple aldehydes and isocyanates.

The synthetic approach to the cyclic 2-azaphosphorinanium salts is outlined in Scheme 1. (4-Aminobutyl)-diphenylphosphine (**2a**), which was easily prepared from a reduction of a corresponding nitrile **1a** in an excellent yield, was treated with 36% hydrochloric acid to give an ammonium salt **3a** quantitatively. Salt **3a** was then treated with bromine and 2 equiv of triethylamine to give a mixture of 2-azaphosphorinanium bromide and triethylammonium halide. A treatment of the mixture with excess lithium perchlorate gave a desired 2-azaphosphorinanium perchlorate **4a** in 61% yield, which was purified by recrystallization from 2-propanol. Similarly, reaction of 3-(diphenylphosphino)propylammonium chloride (**3b**) gave a five-membered 2-azaphospholanium salt **4b** in 61% yield.

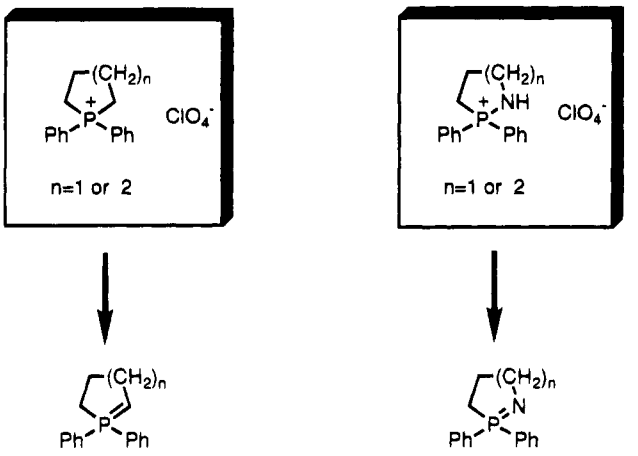

Figure 1.

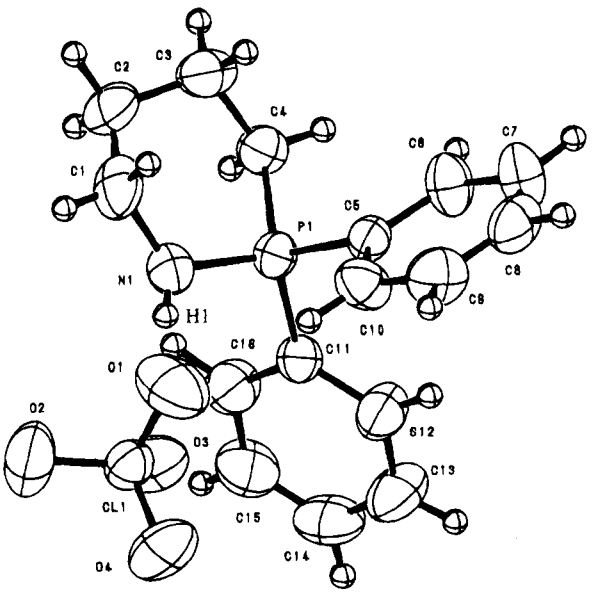

Figure 2. X-ray crystal structure of 1,1-Diphenyl-2-azaphosphorinanium perchlorate (**4a**).

The structure of the 2-azaphosphorinanium salt **4a** was determined by IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectroscopy and elemental analysis and confirmed by X-ray crystal analysis (Figure 2).[10a] In the X-ray analysis, the bond angles of P–C(4)–C(3) and P–N–C(1) are 110.7° and 120.7°, respectively. Campbell and his co-workers

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Scheme 1

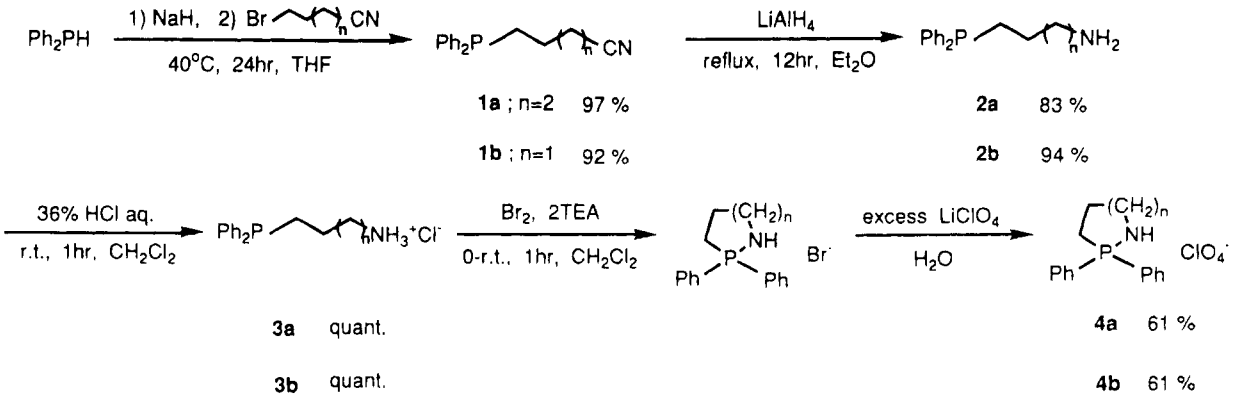


Table 1. Selected Bond Lengths (Å) and Angles (deg)

Bond lengths (Å)	Bond angles (°)
P1–N1 1.620	N1–P1–C4 103.9
N1–C1 1.478	N1–P1–C5 114.2
C1–C2 1.503	N1–P1–C11 107.1
C2–C3 1.511	C4–P1–C5 109.5
C3–C4 1.534	C4–P1–C11 112.7
P1–C4 1.789	C5–P1–C11 109.4
P1–C5 1.790	
P1–C11 1.781	
N1–H1 0.73	P1–N1–C1 120.7
	P1–N1–H1 112.0
	C1–N1–H1 118.0
	P1–N1–C1 120.7
	N1–C1–C2 110.0
	C1–C2–C3 113.3
	C2–C3–C4 111.8
	C3–C4–P1 110.7

Scheme 2

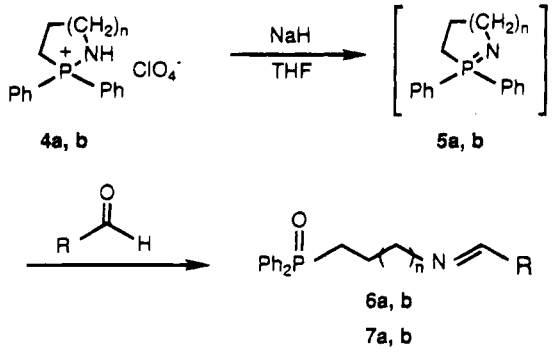


Table 2. Isolated Yields of Imine Derivatives

	yield, %	
R	$n = 2$	$n = 1$
i-Pr	97 (**6a**)	89 (**6b**)
p-$CH_3C_6H_4$	92 (**7a**)	97 (**7b**)

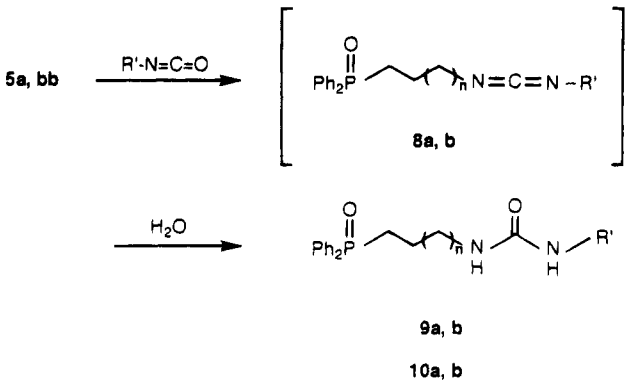
reported[10b] the X-ray analysis of six-membered phosphonium bromide monohydrate which did not contain an endocyclic nitrogen atom, whose P–C–C angles were 109.2–109.8°. The angle of P–C(4)–C(3) in the present work is compatible with those of Campbell's report. On the contrary, the bond angle of P–N–C(1) is agreement with the value of sp^2 hybridization rather than that of a typical tetrahedral angle (Table 1).

Cyclic aza-ylides **5** were readily generated from salts **4** with NaH (Scheme 2). Reaction of **5a,b** with isobutyraldehyde and *p*-tolualdehyde gave imine derivatives in high yield as shown in Table 2. Urea derivatives of **9a,b** and **10a,b** were prepared in good yields (Table 3) by reaction with isopropyl isocyanate and phenyl isocyanate to give the corresponding carbodiimides, which were hydrolyzed to give the urea derivatives (Scheme 3). In the course of the reactions, the characteristic peak on 2260 cm^{-1} of isocyanates completely disappeared and the peak on 2140 cm^{-1} of carbodiimides newly appeared. The resulting products were purified by column chromatography on silica gel.

Table 3. Purified Yields of Urea Derivatives

	yield, %	
R'	$n = 2$	$n = 1$
i-Pr	52 (**9a**)	61 (**9b**)
Ph	74 (**10a**)	50 (**10b**)

Scheme 3



The utilities with which to construct heterocyclic compounds that include a nitrogen atom, for example piperidine and azepine derivatives of cyclic aza-phosphonium salts **4a** and **4b**, are currently being investigated.

Experimental Section

Capillary gas chromatography was performed on a DB-1 megabore column (30 m × 0.53 mm). X-ray crystal analysis was performed by RIGAKU AFC5S.

(3-Cyanopropyl)diphenylphosphine (1a). To a suspension of sodium hydride (60% dispersion in mineral oil, 4.4 g, 110 mmol) in 200 mL of dry THF was added diphenylphosphine[11] (18.6 g, 100 mmol) in 100 mL of dry THF solution at room temperature during 30 min and stirred for 1 h at reflux temperature. To the yellow solution was added a solution of 3-bromopropiononitrile (14.8 g, 100 mmol) in 40 mL of dry THF during 45 min at 45–50 °C and stirred for 24 h at this temperature. After the mixture was quenched with water, the organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 150 mL). The combined organic

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extracts were washed with brine (3 × 200 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give a pale yellow liquid (24.5 g, 97%): IR (neat) 2250 (CN) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.50–2.50 (6H, m), 7.15–7.50 (10H, m); ^{13}C-NMR ($CDCl_3$) δ 18.11 (d, $^2J_{PC}$ = 14.03 Hz), 22.25 (d, $^1J_{PC}$ = 20.14 Hz), 26.99 (d, $^3J_{PC}$ = 14.14 Hz), 118.99 (s), 128.52 (d, $^3J_{PC}$ = 6.71 Hz), 128.75 (s), 132.55 (d, $^2J_{PC}$ = 18.92 Hz), 137.85 (d, $^1J_{PC}$ = 13.43 Hz); MS *m/z* 253 (M^+); HRMS calcd for $C_{16}H_{16}NP$ (M^+) 253.1019, found 253.0987.

(2-Cyanoethyl)diphenylphosphine (1b). Prepared as above. White crystals (6.6 g, 92%): mp 42–43 °C; IR (neat) 2250 (CN) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.25 (2H, s), 2.31 (2H, s), 7.23–7.48 (10H, m); ^{13}C-NMR ($CDCl_3$) δ 14.17 (d, $^1J_{PC}$ = 23.44 Hz), 24.18 (d, $^2J_{PC}$ = 15.63 Hz), 119.39 (d, $^3J_{PC}$ = 14.16 Hz), 128.87 (d, $^3J_{PC}$ = 6.83 Hz), 129.33 (s), 132.75 (d, $^2J_{PC}$ = 19.53 Hz), 136.68 (d, $^1J_{PC}$ = 13.18 Hz); MS *m/z* 239 (M^+); HRMS calcd for $C_{15}H_{14}NP$ (M^+) 239.0862, found 239.0841.

(4-Aminobutyl)diphenylphosphine (2a). To a suspension of lithium aluminum hydride (5.7 g, 150 mmol) in 170 mL of dry diethyl ether was added dropwise a solution of **1** (23.9 g, 94.4 mmol) in 100 mL of dry diethyl ether at a rate such as to produce gentle reflux. After completing the addition, the mixture was refluxed for 18 h. Then, sufficient water was added dropwise and with cooling of the flask in an ice-bath to decompose the excess hydride; 270 g of a 20% solution of sodium potassium tartrate was then added. The clear mixture was transferred to a separatory funnel and after separating the ether layer, the aqueous layer was extracted with ether (2 × 150 mL). The combined organic extracts were washed with brine (3 × 150 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give a pale yellow liquid (20.1 g, 83%): IR (neat) 3360 (NH_2), 3250 (NH_2) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.19 (2H, s), 1.42–1.57 (4H, m), 1.95–2.11 (2H, m), 2.59 (2H, t, J = 6.27 Hz), 7.19–7.51 (10H, m); ^{13}C-NMR ($CDCl_3$) δ 23.45 (d, $^1J_{PC}$ = 16.61 Hz), 28.05 (d, $^3J_{PC}$ = 12.21 Hz), 35.22 (d, $^2J_{PC}$ = 12.21 Hz), 41.80 (s), 128.36 (d, $^3J_{PC}$ = 6.34 Hz), 128.42 (s), 132.71 (d, $^2J_{PC}$ = 18.56 Hz), 139.20 (d, $^1J_{PC}$ = 14.16 Hz); MS *m/z* 257 (M^+); HRMS calcd for $C_{16}H_{20}N_1P_1$ (M^+) 257.1331, found 257.1312.

(3-Aminopropyl)diphenylphosphine (2b). Prepared as above. A pale yellow liquid (34.1 g, 94%): IR (neat) 3360 (NH_2), 3275 (NH_2) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.99 (2H, s), 1.25–1.75 (2H, m), 1.93–2.11 (2H, m), 2.64 (2H, t, J = 6.81 Hz), 7.15–7.49 (10H, m); ^{13}C-NMR ($CDCl_3$) δ 25.49 (d, $^2J_{PC}$ = 12.21 Hz), 30.29 (d, $^1J_{PC}$ = 15.62 Hz), 43.40 (d, $^3J_{PC}$ = 13.65 Hz), 128.35 (s), 128.59 (s), 132.79 (d, $^2J_{PC}$ = 18.55 Hz), 139.09 (d, $^1J_{PC}$ = 14.16 Hz); MS *m/z* 243 (M^+); HRMS calcd for $C_{15}H_{18}N_1P_1$ (M^+) 243.1175, found 243.1163.

4-(Diphenylphosphino)butylammonium Chloride (3a). To a solution of **2a** (19.7 g, 76.6 mmol) in 100 mL of dichloromethane was added 36% HCl aqueous solution (7.8 g, 76.6 mmol) during 10 min and stirred for 1 h at room temperature. This solution was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give white syrup (22.5 g, quantitative): IR (neat) 2600–3200 (NH_3^+) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.20–2.15 (6H, m), 2.70–3.30 (2H, m), 7.28–7.64 (10H, m), 8.28 (3H, bs); ^{13}C-NMR ($CDCl_3$) δ 23.38 (d, $^1J_{PC}$ = 17.58 Hz), 27.59 (d, $^2J_{PC}$ = 11.72 Hz), 28.98 (d, $^3J_{PC}$ = 13.18 Hz), 39.66 (s), 128.37 (s), 128.65 (s), 132.37 (d, $^2J_{PC}$ = 18.56 Hz), 138.56 (d, $^1J_{PC}$ = 12.69 Hz).

(3-Diphenylphosphino)propylammonium Chloride (3b). Prepared as above. White crystals (36.0 g, quantitative): mp 162–167 °C; IR (neat) 2400–3200 (NH_3^+) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.60–2.25 (4H, m), 2.99 (2H, t), 7.21–7.46 (10H, m), 8.20 (3H, bs); ^{13}C-NMR ($CDCl_3$) δ 24.41 (d, $^1J_{PC}$ = 18.07 Hz), 25.22 (d, $^2J_{PC}$ = 13.67 Hz), 40.79 (d, $^3J_{PC}$ = 14.16 Hz), 128.59 (s), 128.89 (s), 132.97 (d, $^2J_{PC}$ = 18.56 Hz), 138.18 (d, $^1J_{PC}$ = 13.18 Hz); MS *m/z* 243 (M^+ – HCl). Anal. Calcd for $C_{15}H_{19}N_1P_1Cl_1$: C, 64.40; H, 6.85; N, 5.01. Found: C, 64.10; H, 6.79; N, 4.97.

1,1-Diphenyl-2-azaphosphorinanium Perchlorate (4a). To a stirred solution of **3a** (8.8 g, 30 mmol) in 120 mL of dry dichloromethane was added dropwise bromine (4.8 g, 30 mmol) at 0–5 °C under nitrogen. The mixture was stirred for 10 min and dry triethylamine (6.1 g, 60 mmol) was added dropwise at 10–15 °C. Then, the mixture was allowed to warm to room temperature and stirred for an additional 1 h. Dichloromethane was evaporated to dryness under reduced pressure to give solid mixture of 1,1-diphenyl-2-azaphosphorinanium halide and triethylammonium halide, which was dissolved ice-cold water, and an excess lithium perchlorate aqueous solution was added. The precipate was filtered and washed with 100 mL of water. The obtained wet solid was dissolved 100 mL of chloroform, and the aqueous layer was separated. The combined organic extracts were dried over anhydrous sodium sulfate and reprecipitated with 150 mL of ethyl acetate or 30 mL of *n*-hexane to afford a crude product which was recrystallized from 2-propanol to give colorless needles (6.4 g, 61%): mp 201–202 °C; IR (neat) 3250 (NH), 1140 (ClO_4) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.82–2.26 (4H, m), 2.55–2.75 (2H, m), 3.25–3.52 (2H, m), 5.29 (1H, d, J_{P-NH} = 3.51 Hz), 7.28–7.95 (10H, m); ^{13}C-NMR ($CDCl_3$) δ 20.53 (d, $^3J_{PC}$ = 7.32 Hz), 21.31 (d, $^1J_{PC}$ = 64.94 Hz), 25.20 (d, $^2J_{PC}$ = 5.86 Hz), 42.41 (d, $^2J_{PC}$ = 3.90 Hz), 121.60 (d, $^1J_{PC}$ = 96.19 Hz), 130.37 (d, $^3J_{PC}$ = 12.69 Hz), 132.50 (d, $^2J_{PC}$ = 11.23 Hz), 135.07 (d, $^4J_{PC}$ = 2.93 Hz); MS *m/z* 254 (M^+ – 2 – ClO_4). Anal. Calcd for $C_{16}H_{19}N_1O_4P_1Cl_1$: C, 54.02; H, 5.38; N, 3.97. Found: C, 54.01; H, 5.38; N, 3.90.

1,1-Diphenyl-2-azaphospholanium perchlorate (4b). Prepared as above. Colorless needles (6.3 g, 61%): mp 160–161 °C; IR (neat) 3325 (NH), 1090 (ClO_4) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.03–2.57 (2H, m), 2.79–3.05 (2H, m), 3.50–3.77 (2H, m), 5.27 (1H, d, J_{P-NH} = 16.70 Hz), 7.44–7.90 (10H, m); ^{13}C-NMR ($CDCl_3$) δ 23.85 (d, $^2J_{PC}$ = 0.98 Hz), 25.66 (d, $^1J_{PC}$ = 64.94 Hz), 47.32 (d, $^2J_{PC}$ = 10.74 Hz), 122.73 (d, $^1J_{PC}$ = 96.68 Hz), 130.13 (d, $^3J_{PC}$ = 13.19 Hz), 132.59 (d, $^2J_{PC}$ = 11.72 Hz), 135.04 (d, $^4J_{PC}$ = 2.93 Hz); MS *m/z* 242 (M^+ – ClO_4). Anal. Calcd for $C_{15}H_{17}N_1O_4P_1Cl_1$: C, 52.72; H, 5.01; N, 4.10. Found: C, 52.73; H, 5.11; N, 4.12.

Diphenyl [4-(isobutylideneamino)butyl]phosphine Oxide (6a). A mixture of sodium hydride (60% dispersion in mineral oil, 90 mg, 2.25 mmol) and 1,1-diphenyl-2-azaphosphorinanium perchlorate (**4a**) (713 mg, 2 mmol) in 10 mL of dry THF was stirred for 1 h at room temperature. After cooling to room temperature, to the mixture was added dropwise isobutyraldehyde (140 mg, 2 mmol) in 5 mL of dry THF solution at room temperature and stirred for 18 h at room temperature. Then, water (20 mL) was added dropwise, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined organic extracts were washed with brine (3 × 50 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give a yellow viscous liquid (630 mg, 97%): IR (neat) 1670 (C=N), 1180 (P=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.99 (6H, m), 1.28–1.79 (4H, m), 2.10–2.31 (3H, m), 3.20–3.50 (2H, m), 7.30–7.95 (11H, m); ^{13}C-NMR ($CDCl_3$) δ 19.22 (d, $^2J_{PC}$ = 6.72 Hz), 19.26 (s), 29.80 (d, $^1J_{PC}$ = 72.02 Hz), 31.95 (d, $^3J_{PC}$ = 14.03 Hz), 33.78 (s), 60.35 (s), 128.60 (d, $^2J_{PC}$ = 9.16 Hz), 130.84 (d, $^3J_{PC}$ = 11.60 Hz), 131.54 (d, $^4J_{PC}$ = 2.44 Hz), 135.98, 169.40 (s); MS *m/z* 327 (M^+); HRMS calcd for $C_{20}H_{26}N_1O_1P_1$ (M^+) 327.1749, found 327.1732.

Diphenyl[3-(isobutylideneamino)propyl]phosphine Oxide (6b). Prepared as above. A yellow syrup (560 mg, 89%): IR (neat) 1670 (C=N), 1180 (P=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.75–2.55 (5H, m), 1.05 (6H, m), 3.31 (2H, m), 7.25–7.90 (11H, m); ^{13}C-NMR ($CDCl_3$) δ 19.34 (s), 23.36 (d, $^2J_{PC}$ = 3.05 Hz), 27.53 (d, $^1J_{PC}$ = 72.63 Hz), 33.94 (s), 61.16 (d, $^3J_{PC}$ = 13.43 Hz), 128.68 (d, $^3J_{PC}$ = 11.60 Hz), 130.91 (d, $^2J_{PC}$ = 9.77 Hz), 131.67 (d, $^4J_{PC}$ = 2.44 Hz), 133.69 (d, $^1J_{PC}$ = 93.39 Hz), 170.41 (s); MS *m/z* 313 (M^+); HRMS calcd for $C_{19}H_{24}N_1O_1P_1$ (M^+) 313.1594, found 313.1584.

Diphenyl[4-[[(*p*-methylphenyl)methylidene]amino]butyl]-phosphine Oxide (7a). Prepared as above. A yellow syrup (690 mg, 92%): IR (neat) 1640 (C=N), 1180 (P=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.28–1.79 (4H, m), 2.18–2.31 (5H, m), 3.48–3.55 (2H, m), 7.10–7.85 (14H, m), 8.15 (1H, s); ^{13}C-NMR ($CDCl_3$) δ 19.60 (d, $^2J_{PC}$ = 4.27 Hz), 21.34 (s), 31.53 (d, $^1J_{PC}$ = 72.02 Hz), 32.03 (d, $^3J_{PC}$ = 14.03 Hz), 60.65 (s), 128.07 (s), 128.56 (d, $^3J_{PC}$ = 9.16 Hz), 129.21 (s), 130.79 (d, $^2J_{PC}$ = 10.99 Hz), 131.49 (d, $^4J_{PC}$ = 3.05 Hz), 133.88 (d, $^1J_{PC}$ = 90.94 Hz), 133.97 (s), 140.56 (s), 160.68 (s); MS *m/z* 375 (M^+); HRMS calcd for $C_{24}H_{26}N_1O_1P_1$ (M^+) 375.1750, found 375.1733.

Diphenyl[3-[[(*p*-methylphenyl)methylidene]amino]-propyl]phosphine Oxide (7b). Prepared as above. A pale yellow crystal (700 mg, 97%): mp 102–107 °C; IR (neat) 1640 (C=N), 1180 (P=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.28–2.49 (4H, m), 2.33 (3H, s), 3.65 (2H, t), 7.13–7.87 (14H, m), 8.19 (1H, s); ^{13}C-NMR ($CDCl_3$) δ 21.37 (s), 23.43 (d, $^2J_{PC}$ = 3.66 Hz), 27.56 (d, $^1J_{PC}$ = 72.63 Hz), 61.35 (s), 128.12 (s), 128.60 (d, $^3J_{PC}$ = 11.60 Hz), 129.29 (s), 130.87 (d, $^2J_{PC}$ = 9.16 Hz), 131.58 (d, $^4J_{PC}$ = 3.05

Hz), 133.73 (d, $^1J_{PC}$ = 94.00 Hz), 133.87 (s), 140.80 (s), 161.36 (s); MS *m/z* 361 (M^+); HRMS calcd for $C_{23}H_{24}N_1O_1P_1$ (M^+) 361.1594, found 361.1607.

***N*-[4-(Diphenylphosphinyl)butyl]-*N'*-isopropyl urea (9a).** A mixture of sodium hydride (60% dispersion in mineral oil, 90 mg, 2.25 mmol) and 1,1-diphenyl-2-azaphosphorinanium perchlorate (**4a**) (713 mg, 2 mmol) in 10 mL of dry THF was stirred for 30 min at room temperature and for 30 min at reflux temperature. After cooling, to this mixture was added dropwise isopropyl isocyanate (170 mg, 2 mmol) in 5 mL of dry THF solution at room temperature and stirred for 3 h at room temperature. Then, water (20 mL) was added dropwise and the solution was stirred for 12 h at reflux temperature. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined organic extracts were washed with brine (3 × 50 mL), dried over anhydrous sodium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography on 100 g of silica gel using ethyl acetate/ethanol (9:1) as eluent to give a white crystal (370 mg, 52%, R_f = 0.35): mp 143–144 °C; IR (neat) 3300 (NH), 1650 (C=O), 1580 (NH) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.03 (6H, d) 1.39–1.77 (4H, m), 2.01–2.44 (2H, m), 2.96–3.23 (2H, m), 3.65–4.02 (1H, m), 5.62 (1H, d), 5.99 (1H, t), 7.35–7.83 (10H, m); ^{13}C-NMR ($CDCl_3$) δ 19.14 (d, $^2J_{PC}$ = 4.82 Hz), 23.54 (s), 29.39 (d, $^1J_{PC}$ = 72.02 Hz), 31.49 (d, $^3J_{PC}$ = 12.82 Hz), 39.38 (s), 41.88 (s), 128.76 (d, $^3J_{PC}$ = 9.16 Hz), 130.84 (d, $^2J_{PC}$ = 11.60 Hz), 131.74 (d, $^4J_{PC}$ = 3.06 Hz), 133.65 (d, $^1J_{PC}$ = 97.66 Hz), 158.68 (s); MS *m/z* 358 (M^+). Anal. Calcd for $C_{20}H_{27}N_2O_2P_1$; C, 67.02; H, 7.59; N, 7.82. Found: C, 66.73; H, 7.60; N, 7.76.

***N*-[3-(Diphenylphosphinyl]propyl]-*N'*-isopropylurea (9b).** Prepared as above. A white crystal (420 mg, 61%, R_f = 0.46, chloroform/ethanol (9:1)): mp 169–170 °C; IR (neat) 3325 (NH), 1640 (C=O), 1560 (NH) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.03 (6H, d), 1.60–1.95 (2H, m), 2.19–2.49 (2H, m), 3.26 (2H, q), 3.66–3.97 (1H, m), 5.59 (1H, d), 6.28 (1H, t), 7.30–7.81 (10H, m); ^{13}C-NMR ($CDCl_3$) δ 23.25 (d, $^2J_{PC}$ = 4.27 Hz), 23.54 (s), 27.55 (d, $^1J_{PC}$ = 72.02 Hz), 40.73 (d, $^3J_{PC}$ = 12.82 Hz), 41.99 (s), 128.84 (d, $^3J_{PC}$ = 9.16 Hz), 130.93 (d, $^2J_{PC}$ = 11.60 Hz), 131.89 (d, $^4J_{PC}$ = 2.44 Hz), 133.50 (d, $^1J_{PC}$ = 97.27 Hz), 158.68 (s); MS *m/z* 344 (M^+); HRMS calcd for $C_{19}H_{25}N_2O_2P_1$ (M^+) 344.1651, found 344.1630.

***N*-[4-(Diphenylphosphinyl)butyl]-*N'*-phenylurea (10a).** Prepared as above. A white crystal (580 mg, 74%, R_f = 0.42, ethyl acetate/ethanol (9:1)): mp 168–169 °C; IR (neat) 3325 (NH), 1640 (C=O), 1560 (NH) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.20–1.70 (4H, m), 2.03–2.40 (2H, m), 3.00–3.30 (2H, m), 6.28–6.34 (1H, t), 6.86–7.79 (15H, m), 8.38 (1H, s); ^{13}C-NMR ($CDCl_3$) δ 19.03 (d, $^2J_{PC}$ = 4.27 Hz), 29.17 (d, $^1J_{PC}$ = 72.02 Hz), 31.20 (d, $^3J_{PC}$ = 13.42 Hz), 39.06 (s), 119.18 (s), 122.06 (s), 128.83 (s), 128.92 (d, $^3J_{PC}$ = 11.60 Hz), 130.80 (d, $^2J_{PC}$ = 9.77 Hz), 131.96 (d, $^4J_{PC}$ = 3.05 Hz), 133.09 (d, $^1J_{PC}$ = 98.27 Hz), 140.34 (s), 156.67 (s); MS *m/z* 392 (M^+). Anal. Calcd for $C_{23}H_{25}N_2O_2P_1$; C, 70.39; H, 6.42; N, 7.14. Found: C, 70.49; H, 6.48; N, 7.03.

***N*-[3-(Diphenylphosphinyl)propyl]-*N'*-phenylurea (10b).** Prepared as above. A white crystal (380 mg, 50%, R_f = 0.57, chloroform/ethanol (9:1)): mp 191–192 °C; IR (neat) 3325 (NH), 1640 (C=O), 1560 (NH) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.64–1.98 (2H, m), 2.09–2.50 (2H, m), 3.28–3.42 (2H, m), 6.70–8.44 (17H, m); ^{13}C-NMR ($CDCl_3$) δ 23.21 (d, $^2J_{PC}$ = 3.66 Hz), 27.34 (d, $^1J_{PC}$ = 72.63 Hz), 40.48 (d, $^3J_{PC}$ = 14.03 Hz), 119.21 (s), 122.03 (s), 129.04 (d, $^3J_{PC}$ = 10.98 Hz), 130.87 (d, $^2J_{PC}$ = 9.16 Hz), 132.13 (d, $^4J_{PC}$ = 2.44 Hz), 135.06, 140.42 (s), 156.65 (s); MS *m/z* 378 (M^+). Anal. Calcd for $C_{22}H_{23}N_2O_2P_1$; C, 69.83; H, 6.13; N, 7.40. Found: C, 69.91; H, 6.23; N, 7.39.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of **1a–4a**, **1b–4b**, **6a,b**, **7a,b**, **9a,b**, and **10a,b** (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ASC; see any current masthead page for ordering information.