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Intermediates in the Diastereoselective Formation of Bis(phosphino)amines

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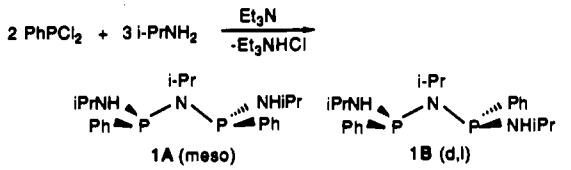
Reaction of *i*-PrNH$_2$ with PhPCl$_2$ and Et$_3$N, which yields *meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$ (**1A**) diastereoselectively, has been examined under conditions which allow isolation of reaction intermediates. PhP(*i*-PrNH)Cl (**2**) and PhP(*i*-PrNH)$_2$ (**3**) are formed stepwise first; subsequent PhPCl$_2$/**2** and PhPCl$_2$/**3** reactions yield *meso*- and *d,l* -*i*-PrN(PhPCl)$_2$ (**4A/4B**) and *erythro*- and *threo*-*i*-PrN[PhP(*i*-PrNH)][PhPCl] (**5A/5B**). *i*-PrNH$_2$ amination of **4A/4B** and **5A/5B** produces the final product **1A**. Diastereomer selection occurs in the *i*-PrNH$_2$/**5A/5B** final reaction step; 1:1 **5A/5B** with *i*-PrNH$_2$ and Et$_3$N yields a 35:1 *meso*:*d,l* mixture of **1**. Reactions of 1:1 **5A/5B** with MeNH$_2$/Et$_3$N, EtNH$_2$/Et$_3$N, *t*-BuNH$_2$/Et$_3$N and PhNH$_2$/Et$_3$N yield a 12:1 *erythro*:*threo* mixture of *i*-PrN[PhP(*i*-PrNH)][PhP(MeNH)] (**7A/7B**), a 24:1 *erythro*:*threo* mixture of *i*-PrN[PhP(*i*-PrNH)][PhP(EtNH)] (**9A/9B**), and monodiastereomers *erythro*-*i*-PrN[PhP(*i*-PrNH)][PhP(*t*-BuNH)] (**12**) and *erythro*-*i*-PrN[PhP(*i*-PrNH)][PhP(PhNH)] (**15**), respectively. The new bis(phosphino)amines are characterized by spectral data; **5A** as the complex *erythro*-*i*-PrN[PhP(*i*-PrNH)][PhPCl]Mo(CO)$_4$ (**6A**) and *erythro*-*i*-PrN[PhP(*i*-PrNH)][PhP(*t*-BuNH)] (**12**) are further characterized by X-ray structural analysis: **6A**, orthorhombic, $P2_12_12_1$, a = 9.5138 (14) Å, b = 15.188 (3) Å, c = 18.200 (45) Å, V = 2629.7 (8) Å^3, Z = 4, R = 0.0271, R_w = 0.0357; **12**, orthorhombic, *Pcba*, a = 10.689 (5) Å, b = 16.294 (7) Å, c = 26.717 (12) Å, V = 4653 (3) Å^3, Z = 8, R = 0.0619, R_w = 0.0630. Mechanistic details of diastereomer selection and correlation of substituent properties with diastereomer selection in the **5A/5B**/RNH$_2$/Et$_3$N reactions (R = Me, Et, *i*-Pr, *t*-Bu, Ph) are discussed.

Introduction

Recently we reported that formation of the bis(phosphino)amine *i*-PrN[PhP(*i*-PrNH)]$_2$ (**1**) from reaction of *i*-PrNH$_2$ with PhPCl$_2$ in the presence of Et$_3$N (eq 1) is highly diastereoselective, strongly



(1)

favoring the *meso*-**1** (**1A**) over the *d,l*-**1** (**1B**) diastereomer.[1] This is the first confirmed example[2,3] of a such a process and it is of interest for several reasons. Most importantly, analogous reaction types might be involved in the chlorophosphine/amine condensation reaction formation of cyclic and acyclic phosphazanes[4] and could ultimately yield stereoregular[5,6] phosph(III)azane polymers. A reaction of the type in eq 1 could be general and therefore useful for the synthesis of other bis(phosphino)amines. Finally, since bis(phosphino)amines analogous to **1** have been postulated,[7] and in some cases observed,[8,9] to be intermediates in the formation of *cis*- and *trans*-diazadiphosphetidines,[10] the role of each diastereomer in four-membered P$_2$N$_2$ ring formation[10,11] could be important to understand.

The stereoselective formation of **1A** over **1B** was clearly established earlier,[1] although the sequence of reactions by which the diastereomers form was not determined. In our initial work, we found that stepwise amination of PhPCl$_2$ yields PhP(*i*-PrNH)Cl (**2**) and PhP(*i*-PrNH)$_2$ (**3**). Other potential intermediates were observed; however, isolation of these or a determination of how they react further to **1A** and **1B** had not been accomplished. Also, it was not clear at which step in the reaction sequence the diastereomer selection process occurs that leads to preferential formation of *meso*-**1** (**1A**). In an attempt to answer these questions, we have continued our study of *i*-PrNH$_2$/PhPCl$_2$ reactions in order to further characterize reaction intermediates and to understand their role in diastereoselective product formation. The results of our work are reported below.

Experimental Section

Apparatus and Materials. All operations were carried out in N$_2$-flushed glove bags and standard vacuum line equipment.[12] Infrared, ^{1}H NMR, and mass spectra were obtained using IBM FTIR (IR/32 Type 9132), Varian VXR 300S (299.9 MHz), and V.G. Analytical 7070 EQ-HF spectrometers, respectively. ^{31}P NMR spectra were obtained on JEOL FX-90Q (36.3 MHz), Bruker WM-250 (101.2 MHz), and Varian VXR 300S (121.4 MHz) spectrometers. ^{1}H and ^{31}P NMR chemical shifts (+δ = downfield) were measured relative to internal Me$_4$Si and external 85% H$_3$PO$_4$, respectively. In cases where relative ^{31}P NMR spectral areas were critical (e.g. **5A**:**5B**, below) the areas measured in decoupled ^{31}P{^{1}H} spectra were compared to undecoupled [^{31}P] spectra while varying the instrumentation conditions over a wide range. In all cases, area agreement was within ±10%. X-ray crystallographic data were collected using a Nicolet Analytical Instruments P3/F automated diffractometer (Mo Kα radiation, graphite monochrometer).

PhP(*i*-PrNH)$_2$ (**3**)[13] and norbornadiene·Mo(CO)$_4$[14] were prepared as described previously. PhPCl$_2$ (Strem Chemicals), Et$_3$N (Baker Chemical), *i*-PrNH$_2$ (Aldrich), *t*-BuNH$_2$ (Aldrich), and PhNH$_2$ (Aldrich) were distilled from CaH$_2$ before use. EtNH$_2$ (Matheson Gas Products) and MeNH$_2$ (Matheson Gas Products) were distilled onto freshly regenerated molecular sieves before use. Toluene (Fisher Scientific) was freshly distilled from Na/Pb alloy.

PhP(*i*-PrNH)Cl (2). *i*-PrNH$_2$ (9.63 g, 163 mmol, 10% excess) in toluene was added dropwise to a toluene solution (125 mL) of PhPCl$_2$ (13.3 g, 74 mmol) at 0 °C. After addition of the amine, the mixture was warmed to room temperature, stirred for 3 h, and then filtered. A slight excess of *i*-PrNH$_2$ was necessary to insure complete conversion of PhPCl$_2$ to PhP(*i*-PrNH)Cl (**2**). The ^{31}P NMR spectrum of the filtrate showed a single resonance at δ 121.1 (**2**)[1] and minor resonances (ca. 5%) at δ 126.0 (area 2), 65.7 (area 1) and 62.8 (area 1) from *i*-PrN[(PhPCl)-(PhP-*i*-PrNH)] (**5A/5B**). The filtrate volume was reduced in vacuo to $^1/_{20}$ the original volume. The resulting mixture showed additional minor ^{31}P NMR signals (ca. 5%) at δ 128.5 and 123.7 from *meso*- and *d,l*-*i*-PrN(PhPCl)$_2$ (**4A/4B**) (see below). Distillation of the mixture yielded

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colorless **2** (bp 52 °C (0.01 mmHg), yield 43%). Anal. Calcd for **2**, $C_9H_{13}PNCl$: mol wt, 201.0474. Found: mol wt (EI$^+$, exact mass), 201.0464. IR (neat, cm^{-1}) 3443 (m), 2969 (s), 1481 (m), 1463 (s), 1434 (s), 1384 (s), 1366 (s), 1307 (m), 1166 (s), 1130 (s), 1019 (s), 997 (s), 883 (s), 746 (s), 697 (s). MS (EI$^+$) *m/e* (% relative intensity) [M$^+$]: 201 (36) [$C_9H_{13}PN^{35}Cl^+$], 203 (10) [$C_9H_{13}PN^{37}Cl^+$]. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 36.3 MHz): δ 121.1 (s). ^1H NMR (C_6D_6, 25 °C, 300 MHz): δ 0.88 (s, br, area 6; CH_3), 2.71 (d, J = 6.8 Hz, area 1; NH), 3.18 (m, area 1; CH), 7.07–7.16 (m, area 4; C_6H_5), 7.75 (t of t, J = 6.4 Hz, J = 1.8 Hz, area 2; C_6H_5). At 90 MHz the δ 0.88 resonance was a pair of doublets (J = 6.4 Hz).

Reactions of 2. (A) With $PhPCl_2/Et_3N$. *i*-PrN(PhPCl)$_2$ (4). Et_3N (10.1 g, 100 mmol) in toluene (20 mL) was added dropwise to a stirred solution of **2** (7.64 g, 38 mmol) and $PhPCl_2$ (6.63 g, 37 mmol) in toluene (100 mL) at 25 °C. Et_3NHCl precipitated slowly from the solution. After 48 h at 25 °C, major ^{31}P NMR signals were present at δ 128.5 and 123.7 [*meso*- (**4A**) and *d,l*-*i*-PrN(PhPCl)$_2$ (**4B**); 1.9:1 ratio]. Resonances at δ 160 ($PhPCl_2$), 125.6 (area 2), 65.7 (area 1), and 62.8 (area 1) (**5A** and **5B**), and a series of doublets at δ 120-130 from uncharacterized higher-order phosphorus products were also present. Typically, **4** represented 50–65% of the total spectral intensity; the ratio **4A**:**4B** = 1.5–1.9:1. Attempts to obtain pure **4A** and **4B** by distillation, crystallization, or chromatography (thin layer or column flash[15]) failed. Characterization data were obtained on a **4A**/**4B**/**2**/$PhPCl_2$ mixture (1.8:1.1:2.0:1.0 m/m). MS (EI$^+$) *m/e* (% relative intensity) [M$^+$]: 347 (0.5) [*i*-PrN($PhP^{37}Cl)_2^+$], 345 (1.5) [*i*-PrN($PhP^{35}Cl$)($PhP^{37}Cl$)$^+$], 343 (2.4) [*i*-PrN($PhP^{35}Cl)_2^+$]. Anal. Calcd for $C_{15}H_{18}NP_2Cl_2$, (M + 1)$^+$: mol wt, 344.0292. Found: mol wt (EI$^+$, exact mass), 344.0300. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 36.3 MHz or 121.4 MHz): δ 128.5 (s, area 3; **4A**) and 123.7 (s, area 2; **4B**); ratio **4A**:**4B** = 1.64:1.00. The ^1H NMR spectrum was complex since the signals for the two diastereomers of **4A** and **4B** could not be analyzed.

A solution of **4A**/**4B** and **2** (mole ratio 4.5:3:2) in toluene, monitored by ^{31}P NMR spectroscopy, was allowed to react with excess S_8 at reflux for 96 h. Although ca. 50% of the reactants were consumed, the reaction mixture was complex and attempts to characterize products failed.

(B) With PhP(*i*-PrNH)$_2$/Et_3N. 2 (3.13 g, 15.6 mmol) in toluene (50 mL) was added to PhP(*i*-PrNH)$_2$ (3.47 g, 15.5 mmol) and Et_3N (21.6 mmol) in toluene (30 mL) at 0 °C. After 6 h, Et_3NHCl was removed by filtration. The reaction solution exhibited ^{31}P NMR spectral singlets at δ 60.1 (**1A**) and 59.1 (**1B**) (area ratio 10:7).

When the reactants were added in the reverse order, PhP(*i*-PrNH)$_2$ (15.5 mmol) in toluene (30 mL) to **2** (3.14 g, 15.6 mmol) and Et_3N (2.19 g, 21.6 mmol) in toluene (50 mL) at 0 °C, **1** was obtained after 6 h (**1A**:**1B** ratio 1:1).

(C) Thermolysis. 2 in toluene (**3**:**4A**:**4B** = 20:3:2 m/m) was heated under N_2 at 95 °C. After 76 h, ^{31}P NMR spectral analysis showed some decomposition of **2**; however, the **4A**:**4B** ratio in the mixture remained at 1.6:1.0.

Reaction of *i*-PrN(PhPCl)$_2$ (4A/4B) with *i*-PrNH$_2$/Et_3N. To a **4A**/**4B** mixture, **4** > 67% (**4A**:**4B** = 1.6:1), in toluene (30 mL) were added *i*-PrNH$_2$ (0.22 g, 3.69 mmol) and Et_3N (0.46 g, 4.5 mmol) in toluene (30 mL). After 1 h, Et_3NHCl was filtered, and the filtrate volume was reduced to $^1/_{10}$ the initial volume in vacuo. ^{31}P NMR spectral analysis showed a **1A**/**1B** mixture (**1A**:**1B** = 27:1).

Reaction of PhP(*i*-PrNH)$_2$ with $PhPCl_2$. *i*-PrN[PhPCl][PhP(*i*-PrNH)] (5A/5B). $PhPCl_2$ (3.83 g, 21.4 mmol) in toluene (25 mL) was added rapidly with stirring to PhP(*i*-PrNH)$_2$ (4.98 g, 22.1 mmol) and Et_3N (2.34 g, 23.1 mmol) in toluene (50 mL) at 0 °C. After 8 h, Et_3NHCl was filtered and the solution was reduced in vacuo to $^1/_4$ its initial volume. ^{31}P NMR spectral analysis of the filtrate showed resonances due to *i*-PrN[PhPCl][PhP(*i*-PrNH)] (**5A**/**5B**) and **2** (**5A**/**5B**:**2** = 3.4:1.0 m/m). Attempts to obtain pure **5** by crystallization, chromatography (thin layer or column flash), and distillation resulted in decomposition to unknown products. $^{31}P\{^1H\}$ NMR (toluene/C_6D_6, 25 °C, 121.4 MHz): δ 126.1 {d, area 1, $^2J_{PP}$ = 10.1 Hz; [PhPCl], **5A**}, 125.8 {d, area 1, $^2J_{PP}$ = 14.2 Hz; [PhPCl], **5B**}, 65.5 {d, area 1, $^2J_{PP}$ = 13.7 Hz; [PhP(*i*-PrNH)], **5B**}, 63.1 {br, area 1, unresolved; [PhP(*i*-PrNH)], **5A**}; ratio of **5A**:**5B** = 1.51:1.00. Anal. Calcd for $C_{18}H_{25}N_2P_2Cl$: mol wt, 366.1182. Found: mol wt, (EI$^+$, exact mass) 366.1162. MS (EI$^+$) *m/e* (% relative intensity) [M$^+$]: 366 (8.4) [*i*-PrN[$PhP^{35}Cl$][PhP(*i*-PrNH)]$^+$], 368 (4.2) [*i*-PrN[$PhP^{37}Cl$][PhP(*i*-PrNH)]$^+$]. IR and ^1H NMR spectra were not clean due to the presence of minor quantities of **2** and **4**. In reactions to produce **5A**/**5B**, small quantities of **4A** and **4B** were also produced when unpurified PhP(*i*-PrNH)$_2$ or excess $PhPCl_2$ was used.

Reactions of *i*-PrN[PhPCl][PhP(*i*-PrNH)] (5A/5B). (A) With Nor·Mo(CO)$_4$. {*i*-PrN[PhPCl][PhP(*i*-PrNH)]}Mo(CO)$_4$ (6A/6B). Nor·Mo(CO)$_4$ (5.40 g, 18.0 mmol) in toluene (70 mL) was added to **5A**/**5B** (6.40 g, 17.5 mmol) in toluene (100 mL) at 0 °C. The solution was filtered, passed through a 2-cm activated alumina column, and then reduced to $^1/_{10}$ its original volume at which time {*i*-PrN[PhPCl][PhP(*i*-PrNH)]}Mo(CO)$_4$ (**6A**/**6B**) crystallized. Recrystallization of the **6A**/**6B** mixture from toluene yielded **6A** (mp 149–152 °C, yield >30%). Anal. Calcd for $MoC_{22}H_{25}N_2P_2ClO_4$: C, 45.97; H, 4.38; N, 4.87; P, 10.78; mol wt, 576.0032. Found: C, 46.03; H, 4.45; N, 4.63; P, 10.54; mol wt (EI$^+$, exact mass), 576.0014. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 36.3 MHz): δ 128.7 [d, $^2J_{PP}$ = 25.6 Hz, area 1; (PhPCl)] and δ 97.9] {d, $^2J_{PP}$ = 25.6 Hz, area 1; [PhP(*i*-PrNH)]}. ^1H NMR (CD_2Cl_2, 25 °C, 300 MHz): δ 0.95 (d, $^3J_{HH}$ = 6.8 Hz, area 2.8; CH_3), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, area 3.0; CH_3), 1.42 (d, $^3J_{HH}$ = 6.4 Hz, area 3.0; CH_3), 1.45 (d, $^3J_{HH}$ = 6.4 Hz, area 3.0; CH_3), 2.74 (d of d, $^2J_{PH}$ = 6.4, $^3J_{HH}$ = 9.6 Hz, area 1.1; *i*-PrNH), 3.46 (d of d of septets, $^3J_{HH}$ = 6.8 Hz, area 1.2; Me_2CHN), 4.00 (d of d of septets, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 9.6 Hz, area 1.1; Me_2CHNH), 7.47–7.53 (m, area 3.0; C_6H_5), 7.57–7.62 (m, area 3.0; C_6H_5), 7.61–7.69 (m, area 1.9; C_6H_5), 8.06–8.14 (m, area 1.9; C_6H_5). IR (KBr, cm^{-1}): 3372 (m), 2966 (w), 2028 (vs), 1922 (br), 1861 (vs), 1135 (m), 1037 (s), 859 (m), 835 (m), 610 (s), 577 (s), 532 (w), 511 (m), 476 (m), 459 (w), 418 (w). MS (EI$^+$) *m/e* [M$^+$]: 576 [$MoC_{22}H_{25}N_2P_2ClO_4^+$]. From a **6A**/**6B** mixture, $^{31}P\{^1H\}$ NMR (toluene/C_6D_6) data for **6B** were obtained: δ 130.7 [d, $^2J_{PP}$ = 37.8 Hz, area 1; (PhPCl)], 100.0 {d, $^2J_{PP}$ = 37.8 Hz, area 1; [PhP(*i*-PrNH)]}.

(B) With *i*-PrNH$_2$/Et_3N. To a stirred solution of **5A**/**5B** (6.59 g, 18 mmol) at 0 °C were added *i*-PrNH$_2$ (1.72 g, 29 mmol) and Et_3N (2.83 g, 28 mmol) in toluene (15 mL) dropwise. After addition, ^{31}P NMR spectral analysis showed complete conversion of **5A**/**5B** to a **1A**/**1B** mixture (**1A**:**1B** = 30–35:1). After removal of the toluene in vacuo, **1A** precipitated from the solution. Recrystallization from decane yielded **1A** (mp = 101–103 °C, yield 73%). The ^{31}P NMR, ^1H NMR, and mass spectra are identical to those previously reported.[1]

An *i*-PrNH$_2$/**5A**/**5B** reaction identical to that above was carried out, but without Et_3N. ^{31}P NMR spectral analysis showed formation of **1A**/**1B** (**1A**:**1B** = 10–12:1).

(C) With MeNH$_2$/Et_3N. *i*-PrN[PhP(*i*-PrNH)][PhP(MeNH)] (7A/7B). $MeNH_2$ (0.36 g, 11.6 mmol) was condensed into a degassed solution of **5A**/**5B** (3.48 g, 9.5 mmol) and Et_3N (1.48 g, 14.4 mmol) in toluene (40 mL) at −78 °C. The solution was warmed to room temperature and stirred. After 12 h, Et_3NHCl was filtered and the solution volume reduced in vacuo to $^1/_{10}$. Analysis of the concentrated filtrate showed spectral data for *i*-PrN[PhP(*i*-PrNH)][PhP(MeNH)] (**7A**/**7B**) (**7A**:**7B** = 12.4:1) and minor quantities of PhP(MeNH)(*i*-PrNH) (**8**, δ 60.5) (<20% of total spectral area). **7A**/**7B** could not be separated by crystallization, chromatography (thin layer or flash), or distillation. Anal. Calcd for $C_{19}H_{29}N_3P_2$: mol wt, 361.1837. Found: mol wt (EI$^+$, exact mass), 361.1816. MS *m/e* (% relative intensity) [M$^+$]: EI$^+$, 361 (4.6) [$C_{19}H_{29}N_3P_2^+$]; CI$^+$, 362 (30) [$C_{19}H_{30}N_3P_2^+$]. $^{31}P\{^1H\}$ NMR (121.1 MHz) of the filtrate (**7**:**8** = 6:1 m/m): δ 68.3 {d, $^2J_{PP}$ = 13.4; [PhP(MeNH)] (**7A**)}, 60.5 {d, $^2J_{PP}$ = 13.4 Hz; [PhP(*i*-PrNH)] (**7A**)}, 58.8 {d, $^2J_{PP}$ = 8.6 Hz; [PhP(*i*-PrNH)] (**7B**)} and 63.5 [s; **8**]. The ^1H NMR spectra were too complicated to interpret due to impurities in the samples.

(D) With EtNH$_2$/Et_3N. *i*-PrN[PhP(*i*-PrNH)][PhP(EtNH)] (9A/9B). $EtNH_2$ (0.34 g, 7.4 mmol) was condensed into a degassed solution of **5A**/**5B** (2.5 g, 6.9 mmol) and Et_3N (1.53 g, 15.1 mmol) in toluene (30 mL) at −78 °C. Et_3NHCl was filtered and the solution volume reduced to $^1/_{10}$ in vacuo. ^{31}P NMR spectral analysis of the filtrate showed resonances for *i*-PrN[PhP(*i*-PrNH)][PhP(EtNH)] (**9A**/**9B**) (**9A**:**9B** = 23.5:1) and minor resonances (<10%) at δ 61.1 (**10**) and 65.1 (**11**). Upon concentration of the solution to $^1/_{20}$ its original volume, **9A** precipitated. Recrystallization from toluene yielded **9A** (mp = 84–88 °C, yield >65%). Anal. Calcd for $C_{20}H_{31}N_3P_2$: C, 63.98; H, 8.32; N, 11.19; P, 16.50; mol wt, 375.1993. Found: C, 63.97; H, 8.47; N, 11.07; P, 16.23; mol wt (EI$^+$, exact mass), 375.1978. IR (KBr, cm^{-1}): 3317 (w), 3059 (w), 2966 (s), 1124 (s), 999 (m), 866 (s), 844 (vs), 743 (vs), 700 (s), 476 (s). MS (EI$^+$) *m/e* (% relative intensity) [M$^+$]: 375 (5) [$C_{20}H_{31}N_3P_2^+$]. $^{31}P\{^1H\}$ NMR (10% C_6D_6, 36.3 MHz): δ 64.6 {d, $^2J_{PP}$ = 14.6 Hz, area 1; [PhPEtNH]} and 60.5 {d, $^2J_{PP}$ = 14.6 Hz, area 1; [PhP(*i*-PrNH)]}. ^1H NMR (10% toluene-d_8, 22 °C, 300 MHz): δ 0.98 (t, $^3J_{HH}$ = 7.08 Hz, area 3; CH_2CH_3), 1.01 (d, $^3J_{HH}$ = 6.10 Hz, area 3; CH_3), 1.07 (d, $^3J_{HH}$ = 6.59 Hz, area 3; CH_3), 1.31 (d, $^3J_{HH}$ = 6.59 Hz, area 3; CH_3), 1.32 (d, $^3J_{HH}$ = 6.35 Hz, area 3; CH_3), 2.08 (m, area 1; $NHCH_2$), 2.14 (d of d, $^3J_{PH}$ = 13.92 Hz, $^3J_{HH}$ = 4.88 Hz, area 1; NHCH), 2.80, 2.92, 3.13 (m, area 4; two $CHMe_2$ and CH_2Me), 7.14 (t, J = 7.33 Hz, area 2; C_6H_5), 7.26 (t of t, J = 7.33 Hz, J = 1.50 Hz, area 4; C_6H_5), 7.70 (m, area 4; C_6H_5). A $^{31}P\{^1H\}$ NMR spectral study (toluene/benzene-d_6, 25 °C, 121.4 MHz) of the filtrate gave spectral data for **9B**: δ 60.9 {d, $^2J_{PP}$ = 12.6 Hz; [PhP(*i*-PrNH)]}, 59.6 {d, $^2J_{PP}$ = 6.9 Hz; [PhP(*i*-PrNH)]}.

(15) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 1986.

(E) With t-BuNH$_2$/Et$_3$N. i-PrN[PhP(i-PrNH)][PhP(t-BuNH)] (12). $tert$-BuNH$_2$ (3.62 g, 49.5 mmol) and Et$_3$N (4.95 g, 48.9 mmol) in toluene (30 mL) were added dropwise to a solution of **5A/5B** (17.5 mmol) in toluene (55 mL) at 0 °C. After 2 days at room temperature, Et$_3$NHCl was filtered off. The filtrate showed ^{31}P NMR resonances (101.2 MHz) for i-PrN[PhP(i-PrNH)][PhP(t-BuNH)] (**12**) and minor resonances at δ 49.0 (**13**) and 50.6 (**14**); **12**:**13**:**14** = 16.5:1.0:1.0 m/m. Recrystallization from toluene yielded **12** (mp = 90–95 °C, yield >70%). Anal. Calcd for $C_{22}H_{35}N_3P_2$: C, 65.48; H, 8.74; N, 10.41; P, 15.35; mol wt, 403.2306. Found: C, 65.50; H, 8.79; N, 10.45; P, 14.79; mol wt (EI$^+$ exact mass), 403.2301. ^{31}P{^{1}H} NMR (toluene/C_6D_6): δ 62.4 [d, $^2J_{PP}$ = 14.7 Hz, area 1; [PhP(i-PrNH)]], 49.2 [d, $^2J_{PP}$ = 14.6 Hz, area 1; [PhP(t-BuNH)]]. ^{1}H NMR (10% in toluene-d_8, 22 °C, 300 MHz): δ 0.89 (d, $^3J_{HH}$ = 6.1 Hz, area 3; CH$_3$), 1.00 (d, $^3J_{HH}$ = 6.4 Hz, area 3; CH$_3$), 1.19 [s, area 9; C(CH$_3$)$_3$], 1.29 (d, $^3J_{HH}$ = 6.6 Hz, area 3; CH$_3$), 1.36 (d, $^3J_{HH}$ = 6.6 Hz, area 3; CH$_3$), 1.98 [d of d, $^2J_{PH}$ = 11.7 Hz, $^3J_{HH}$ = 2.9 Hz, area 1; N*H*(i-Pr)], 2.54 [d, $^2J_{PH}$ = 11.0 Hz, area 1; NH(t-Bu)], 2.91 [d of d of q of q, $^3J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 6.1 Hz, $^2J_{PH}$ = 11.7 Hz, area 1; NC*H*(CH$_3$)$_2$], 3.10 [d of septets, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 3.7 Hz, area 1; NHC*H*(CH$_3$)$_2$], 7.11–7.16 (m, area 2; C$_6$H$_5$), 7.23–7.31 (m, area 4; C$_6$H$_5$), 7.72–7.80 (m, area 4; C$_6$H$_5$). IR (KBr, cm^{-1}) 2954 (s), 1459 (m), 1368 (s), 1225 (s), 1163 (m), 1135 (m), 996 (vs), 866 (vs), 853 (vs), 749 (vs), 701 (s), 588 (w), 533 (m), 516 (w), 473 (w), 422 (w). MS m/e (% relative intensity) [M$^+$]: EI$^+$, 403 (1.6) [$C_{22}H_{35}N_3P_2^+$]; CI$^+$, 404 (100) [$C_{22}H_{36}N_3P_2^+$].

(F) With PhNH$_2$/Et$_3$N. i-PrN[PhP(i-PrNH)][PhP(PhNH)] (15). Aniline (1.97 g, 21.2 mmol) and Et$_3$N (2.16 g, 21.3 mmol) in toluene (25 mL) were added dropwise to a solution of **5A/5B** (16.2 mmol) in toluene (50 mL) at 0 °C. After 24 h, ^{31}P NMR analysis of the filtrate showed major signals for i-PrN[PhP(i-PrNH)][PhP(PhNH)] (**15**) and a minor signals at 52.4 (**16**) (**15**:**16** = 18.2:1 m/m). Recrystallization from toluene gave pure **15** (mp = 93–95 °C, yield >80%). Anal. Calcd for $C_{24}H_{31}P_2N_3$: C, 68.06; H, 7.39; N, 9.92; P, 14.64. Found: C, 67.06; H, 7.46; N, 9.74; P, 14.75. ^{31}P{^{1}H} NMR (toluene/C_6D_6, 36.3 MHz): δ 62.8 [d, $^2J_{PP}$ = 12.2 Hz, area 1; [PhP(i-PrNH)]], 54.7 (d, $^2J_{PP}$ = 12.2 Hz, area 1; [PhP(PhNH)]). ^{1}H NMR (CD_2Cl_2): δ 1.04 (d, J = 6.4 Hz, area 3; CH$_3$), 1.22 (d, J = 6.4 Hz, area 3; CH$_3$), 1.23 (d, J = 6.1 Hz, area 3; CH$_3$), 1.4 (d, J = 6.35 Hz, area 3; CH$_3$), 2.33 (d of d, J = 11.7 Hz, J = 6.4 Hz, J = 6.1 Hz, area 1, i-PrNH), 3.18 (m, area 2; NHC*H*Me$_2$), 3.25 (m, area 1; NC*H*Me$_2$), 5.05 (d, $^2J_{PP}$ = 9.5 Hz, area 1; PhNH), 6.79–7.72 (m, area 15; C$_6$H$_5$). IR (KBr, cm^{-1}): 3350 (w), 3035 (m), 1957 (s), 1232 (m), 996 (vs), 933 (vs), 780 (m). MS m/e (% relative intensity) [M$^+$]: EI$^+$, 423 (3.1) [$C_{24}H_{31}P_2N_3^+$]; CI$^+$, 424 (21.6) [$C_{24}H_{32}P_2N_3^+$].

(G) With Et$_3$N. Et$_3$N (1.09 g, 10.8 mmol) was added to a solution of **5A/5B**, **4A/4B**, and **2** (**5**:**4**:**2** = 7.3:1.0:2.0 m/m) (7.4 mmol) in toluene. After 12 h, ^{31}P NMR spectral resonances appeared at δ 166.4 and 92.1. The resonance for **2** had disappeared. The reaction went to ca. 40% completion; resonances for **5A/5B** and **4A/4B** were still present after 60 h. After 2 days at 60 °C, no further spectral changes were observed.

{i-PrN[PhP(i-PrNH)][PhP(t-BuNH)]}Mo(CO)$_4$ (17). Nor·Mo(CO)$_4$ (0.63 g, 2.1 mmol) was dissolved in toluene (25 mL) and cannulated into a solution of **12** (0.77 g, 1.9 mmol) in toluene (50 mL) at 0 °C. The mixture was warmed to room temperature, filtered, and passed through a 2-cm activated alumina column. Recrystallization gave **17** (mp 180–183 °C). Anal. Calcd for **17**, $MoC_{26}H_{35}N_3P_2O_4$: C, 51.07; H, 5.77; N, 6.87; mol wt, 613.1157. Found: C, 66.36; H, 9.16; N, 3.87; mol wt (EI$^+$ exact mass), 613.1130. ^{31}P{^{1}H} NMR (toluene/C_6D_6, 101.5 MHz): δ 93.2 [d, $^2J_{PP}$ = 35.5 Hz, area 1, [(PhP-i-PrNH)-i-PrN]], 85.4 [d, $^2J_{PP}$ = 36.1 Hz, area 1, [(PhP-i-BuNH)-i-PrN]]. MS (EI$^+$), M$^+$, m/e 613.

X-ray Structure Analyses. (A) {i-PrN(PhPCl)[PhP(i-PrNH)]}Mo(CO)$_4$ (6A). A crystal from toluene was mounted on a glass fiber and coated with epoxy resin. Crystal data and details of the data collection and structure refinement are summarized in Table I. Unit cell parameters were determined on the diffractometer and refined by least-squares fit to 25 centered reflections in the range 27.2° ≤ 2θ ≤ 34.5°. The structure was solved using Patterson techniques. The molecule was refined anisotropically except for the hydrogen atoms, which were included in idealized positions with fixed isotropic displacement parameters. Amine hydrogens refined into positions corresponding to sp^2 hybridization and therefore were included in idealized positions. The methine proton [(CH$_3$)$_2$C*H*] on the central i-PrN group could not be located. Attempts to account for this hydrogen atom discrepancy in the refinement of the structure by employing partial occupancy for the methyl groups was unsuccessful. The final model was refined without the methine hydrogen. Final positional parameters for **6A** are given in Table II. Thermal parameters are included in the supplementary material.

(B) i-PrN[PhP(i-PrNH)][PhP(t-BuNH)] (12). A crystal from toluene was mounted on a glass fiber and coated with epoxy resin. Crystal data and details of the data collection and structure refinement are summarized in Table I. Unit cell parameters were determined on the diffractometer and refined by least squares fit to 25 centered reflections in the range 32.2° ≤ 2θ ≤ 35.0°. The structure was solved by direct methods. The molecule was refined anisotropically except for the hydrogen atoms, which were included in idealized positions. Amine hydrogens refined into positions corresponding to sp^2 hybridization and therefore were included in idealized positions. Final positional parameters for **12** are given in Table III. Thermal parameters are included in the supplementary material.

Table I. Crystallographic Data for i-PrN[PhPCl][PhP(i-PrNH)]Mo(CO)$_4$ (**6A**) and i-PrN[PhP(t-BuNH)][PhP(i-PrNH)] (**12**)

	6A	**12**
formula	$C_{22}H_{25}N_2P_2ClO_4Mo$	$C_{22}H_{35}N_3P_2$
mol wt	574.8	403.23
space group	$P2_12_12_1$	$Pcba$
a, Å	9.5138 (14)	10.689 (5)
b, Å	15.188 (3)	16.294 (7)
c, Å	18.200 (5)	26.717 (12)
vol, Å^3	2629.7 (8)	4653 (3)
d_{calc}, g cm^{-3}	1.452	1.152
Z	4	8
F(000), e$^-$	1168	1744
temp, °C	22–26	−100
λ(Mo Kα), Å	0.710 73	0.710 73
μ(Mo Kα) cm^{-1}	7.4	1.93
transm coeff	0.746, 0.741	none
R	0.0271	0.0619
R_w	0.0357	0.0630

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for i-PrN[PhPCl][PhP(i-PrNH)]Mo(CO)$_4$ (**6A**)

	x	y	z	U_{eq}[a]
Mo(1)	1705 (1)	9451 (1)	7626 (1)	40 (1)
Cl(1)	3427 (1)	11685 (1)	7210 (1)	66 (1)
P(1)	2931 (1)	9875 (1)	8803 (1)	42 (1)
P(2)	3804 (1)	10370 (1)	7476 (1)	43 (1)
N(1)	2221 (4)	10520 (2)	9429 (2)	52 (1)
N(2)	4328 (4)	10381 (2)	8354 (2)	46 (1)
O(1)	−270 (4)	11133 (2)	7411 (2)	80 (1)
O(2)	−980 (4)	8468 (3)	8209 (3)	99 (2)
O(3)	3152 (5)	7594 (3)	7642 (3)	119 (2)
O(4)	1217 (4)	8985 (3)	5974 (2)	80 (1)
C(17)	918 (5)	11021 (3)	9351 (3)	61 (2)
C(27)	5543 (6)	10877 (4)	8651 (4)	92 (3)
C(1)	459 (4)	10546 (3)	7507 (2)	53 (2)
C(2)	1 (6)	8811 (3)	7996 (3)	57 (2)
C(3)	2693 (5)	8281 (3)	7654 (3)	66 (2)
C(4)	1350 (5)	9172 (3)	6585 (3)	53 (2)
C(18)	129 (6)	11020 (5)	10044 (3)	92 (3)
C(19)	1204 (7)	11955 (4)	9087 (4)	100 (3)
C(28)	5262 (7)	11671 (5)	9028 (4)	123 (4)
C(29)	6835 (7)	10449 (6)	8677 (5)	151 (4)
C(11)	3815 (5)	9063 (3)	9386 (2)	46 (1)
C(12)	4918 (6)	8577 (4)	9104 (3)	69 (2)
C(13)	5581 (6)	7944 (4)	9523 (3)	76 (2)
C(14)	5163 (6)	7802 (4)	10224 (3)	72 (2)
C(15)	4102 (6)	8268 (3)	10517 (3)	65 (2)
C(16)	3414 (6)	8899 (3)	10103 (2)	57 (2)
C(21)	5368 (5)	10175 (3)	6930 (2)	56 (2)
C(22)	5996 (6)	10770 (4)	6473 (3)	86 (2)
C(23)	7208 (8)	10527 (7)	6094 (4)	126 (4)
C(24)	7754 (7)	9696 (8)	6157 (5)	134 (5)
C(25)	7112 (7)	9113 (6)	6598 (4)	116 (4)
C(26)	5940 (6)	9323 (4)	6983 (3)	80 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

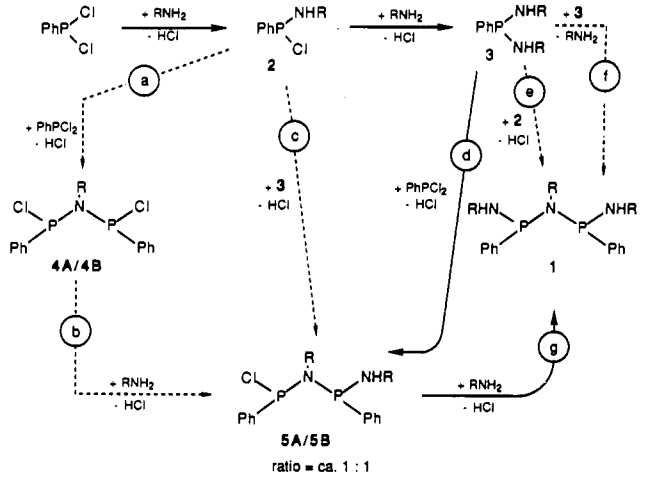
Studies of i-PrNH$_2$/PhPCl$_2$ reactions and reactions involving the first-formed intermediates PhP(i-PrNH)Cl (**2**) and PhP(i-PrNH)$_2$ (**3**), have allowed us to identify intermediate bis(phos-

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for *i*-PrN[PhP(*t*-BuNH)][PhP(*i*-PrNH)] (**12**)

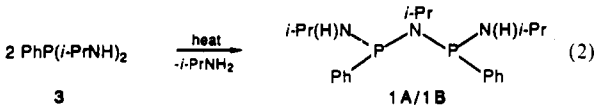
	x	*y*	*z*	U_{eq}[a]
P(1)	−678 (1)	2771 (1)	3524 (1)	29 (1)
P(2)	372 (1)	4404 (1)	3798 (1)	29 (1)
N(1)	530 (3)	2595 (2)	3143 (1)	38 (1)
N(2)	−173 (3)	3458 (2)	3970 (1)	31 (1)
N(3)	−327 (3)	5112 (2)	4155 (1)	41 (1)
C(11)	−1659 (3)	3463 (2)	3146 (1)	29 (1)
C(12)	−2731 (4)	3775 (3)	3374 (2)	41 (1)
C(13)	−3564 (4)	4255 (3)	3107 (2)	50 (2)
C(14)	−3345 (5)	4434 (3)	2608 (2)	48 (1)
C(15)	−2285 (4)	4124 (3)	2382 (2)	44 (1)
C(16)	−1454 (4)	3631 (2)	2645 (2)	36 (1)
C(17)	1066 (4)	1797 (2)	3000 (2)	42 (1)
C(18)	293 (5)	1102 (3)	3191 (3)	74 (2)
C(19)	2382 (5)	1732 (3)	3204 (2)	68 (2)
C(20)	1157 (7)	1750 (3)	2436 (2)	76 (2)
C(21)	1940 (4)	4389 (2)	4085 (1)	33 (1)
C(22)	2481 (5)	5068 (3)	4310 (2)	43 (1)
C(23)	3721 (5)	5057 (3)	4456 (2)	56 (2)
C(24)	4429 (4)	4371 (3)	4383 (2)	54 (2)
C(25)	3925 (4)	3690 (3)	4158 (2)	46 (1)
C(26)	2693 (4)	3697 (3)	4008 (2)	38 (1)
C(27)	−214 (4)	3201 (2)	4506 (2)	35 (1)
C(28)	−1541 (4)	3197 (3)	4705 (2)	48 (1)
C(29)	421 (5)	2376 (3)	4593 (2)	46 (1)
C(37)	−1234 (4)	5704 (2)	3963 (2)	40 (1)
C(38)	−703 (5)	6560 (3)	3956 (2)	60 (2)
C(39)	−2440 (5)	5677 (3)	4255 (2)	66 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme I

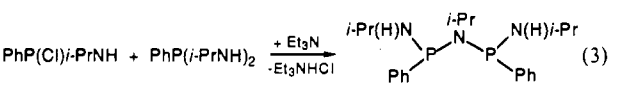


phino)amines *i*-PrN(PhPCl)$_2$ (**4**) and *i*-PrN[PhP(*i*-PrNH)](PhPCl) (**5**) (Scheme I) as species which can form en route to **1**. The possible interrelationships of these species in the formation of **1** are summarized in Scheme I. From reactions involving **2**–**5** under conditions of carefully controlled reaction time, temperature, and reactant ratios, we can assess the relative role of the four intermediates in the diastereomeric formation of **1**. We had shown previously that formation of **1A** from **3** via loss of RNH_2 (eq 2; step f) occurs nondiastereoselectively and only with difficulty.[1]



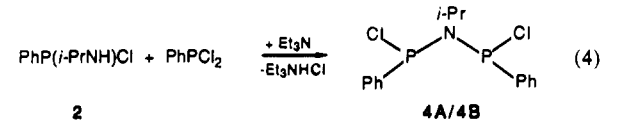
Therefore it was of interest to concentrate on those reactions which involved phosphorus–nitrogen bond formation through elimination of HCl.

Compound **2** could lead to **1** by several routes; directly through a **2**/**3** reaction (step e) or through the formation of bis(phosphino)amine intermediates (steps a or c). The possibility that **2** and **3** in the presence of Et_3N could form **1** (eq 3) was examined



in reactions carried out under conditions as close as possible to those which might exist during the *i*-PrNH$_2$/PhPCl$_2$ reaction, i.e. **2** in excess as expected early in the reaction or, conversely, with **3** in excess as would occur late in the reaction. In both cases, diastereomers **1A** and **1B** formed in an approximately 1:1 mole ratio. No diastereoselectivity was observed. Thus, the **2**/**3** reaction path appears unimportant in the **1A** formation process.

Reaction between **2** and PhPCl$_2$ (step a) in the presence of Et_3N at 25 °C during 12–24 h yields the bis(phosphino)amine intermediate **4A**/**4B** as in (eq 4). However, the reaction is much

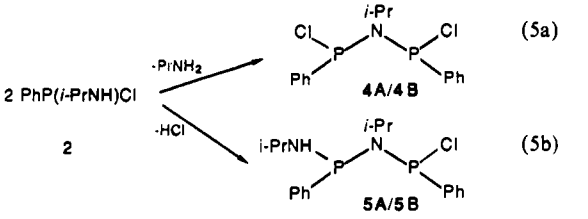


slower, ca. 12–24 h vs 0.5 h, than the *i*-PrNH$_2$/PhPCl$_2$/Et_3N diastereoselective reaction (eq 1). The **2**/PhPCl$_2$ reaction is relatively clean (products, >60 mol % **4A**/**4B**); however, under all conditions examined reaction products included small amounts of **2**, bis(phosphino)amines **5A**/**5B**, and traces of higher order phosphorus products which could not be isolated.

Attempts to isolate **4A**/**4B** from the reaction mixture by high-vacuum distillation resulted in its decomposition. Isolation of **4A**/**4B** by crystallization or chromatography (thin layer and flash) were also unsuccessful. Finally, reactions of **4A**/**4B** with sulfur were attempted in order to obtain crystallizable sulfide; however, only a mixture of indefinite composition was obtained. Thus, characterization of **4A**/**4B** is based on ^{31}P NMR and mass spectral (EI$^+$ and EI$^+$ exact mass) data obtained on samples which contained mostly **4** (>65%). The two ^{31}P NMR resonances for the *meso* and *d,l* diastereomers of *i*-PrN(PhPCl)$_2$ (**4A** and **4B**) at δ 128.5 and 123.7 typically occur in a 1.5–1.9:1 ratio. These fall in the region expected for aminochlorophenylphosphines.[16] The mass spectrum of **4A**/**4B** showed a distinct, characteristic parent ion at *m*/*e* 343. **4A**/**4B** was not obtained sufficiently pure to allow reliable ^1H NMR spectral or chemical elemental analysis.

The reaction of *i*-PrNH$_2$ and Et_3N with **4A**/**4B** was examined in order to demonstrate further the composition of **4A**/**4B** and its role in **1A**/**1B** formation. The reaction yields **1A** and **1B**, typically in a ratio of ca. 27:1. Even though this reaction does produce **1A** diastereoselectively, **4A**/**4B** forms so slowly relative to the rate of formation of **1** (12–24 h vs 0.5 h) that it appears that the reaction path which involves steps a, b, g (Scheme I) is not the major path for diastereoselective formation of **1A** from reaction of PhPCl$_2$ with *i*-PrNH$_2$.

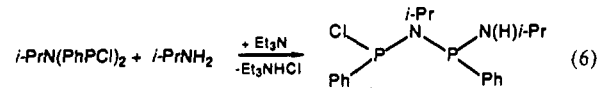
Thermolysis of **2** was studied, in the absence of Et_3N, to determine if either **4A**/**4B** or **5A**/**5B** could be obtained by simple *i*-PrNH$_2$ (eq 5a) or HCl (eq 5b) elimination, respectively. **2**, in



a **2**/**4** mixture, was heated at 95 °C for 3 days under N_2. No reaction occurred. In addition, it was observed that the **4A**:**4B** ratio remained unchanged during the thermolysis. Since the diastereomers do not racemize at elevated temperatures, it seems likely that the **4A**:**4B** ratio is determined thermodynamically, not kinetically.

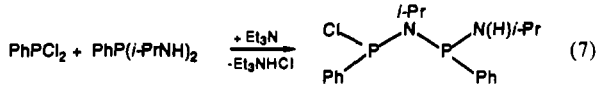
(16) Keat, R. *J. Chem. Soc., Dalton Trans.* **1976**, 1424.

Although **1A** must not form primarily from **4A/4B**, because the latter forms only slowly in the $2/PhPCl_2/Et_3N$ reaction (step a), the **4A/4B** reaction with *i*-$PrNH_2$ to produce **1A** stereoselectively suggests that the reaction proceeds through the key unsymmetrical bis(phosphino)amine intermediate **5A/5B** (eq 6). This essential role played by **5A/5B** was confirmed in studies of its formation and subsequent reaction with *i*-$PrNH_2$.



(6)

Bis(phosphino)amines **5A/5B** form rapidly (ca. 0.5 h) in reactions of **3** with $PhPCl_2$ (1:1 ratio, m/m) and excess Et_3N (eq 7, step d). The product is generally contaminated with small



(7)

amounts of **2** and other material (<5%). Attempts to isolate **5A/5B** from the mixture by distillation, crystallization, and chromatography (flash and thin layer) were unsuccessful. Both **5A/5B** and **2** in the mixture appeared to react with the silica gel during chromatography to form uncharacterized products.

Characterization of **5A/5B** is based on ^{31}P NMR (36.3 and 121.1 MHz) and mass spectral (EI^+ and EI^+ exact mass) data. Also, indirect characterization is obtained from single-crystal X-ray data analysis of the $Mo(CO)_4$ complex **6A/6B** (below). The 121.1-MHz ^{31}P NMR spectrum shows two sets of doublets at δ 126.1 and 125.8 for the [PhP(Cl)-*i*-PrN] and two doublets at δ 65.5 ppm ($^2J_{PP}$ = 13.7 Hz) and 63.1 ppm ($^2J_{PP}$ = 8.0 Hz) for the [PhP(*i*-PrNH)-*i*-PrN] phosphorus moieties of the diastereomers. Comparison of the ^{31}P NMR data with those of previously reported amino- and aminochloroalkylphosphines provides unambiguous characterization, even though unsymmetrical bis(phosphino)amine analogues are not known. The PhP(Cl)NR units of **2**, PhP(Cl)-*t*-BuNH,[1,16,17] *n*-PrN[(PhPCl)(PPh_2)],[17] *i*-PrN[(PhPCl)-(PPh_2)],[16,17] and $MeN(PhPCl)_2$[3] have ^{31}P NMR chemical shifts in the range δ 116.5–137.1, close to the low-field resonances of **5A/5B**. Resonances for **1A**, **3**, $PhP(EtNH)_2$,[1] and PhP(*t*-$BuNH)_2$,[1] are at δ 41.1–60.1, close to the high-field resonances of **5A/5B**. The **5A**:**5B** ratio typically ranged from 1.5–1.2:1. Except for **2**, the other minor resonances in the product mixture were not characterized. The presence of **2** in the product mixtures might be the result of *i*-PrNH–Cl group exchange between $PhPCl_2$ and $PhP(i\text{-}PrNH)_2$; such exchange occurs with other phosphorus(III)–nitrogen compounds.[10]

Derivatization of **5A/5B** by reaction with nor-$Mo(CO)_4$ quantitatively yields the complex {*i*-PrN[PhPCl][PhP(*i*-PrNH)]}$Mo(CO)_4$ (**6A/6B**). **6A** and **6B** crystallize from toluene; recrystallization products X-ray quality crystals of **6A**. Pure **6B** was not obtained. The ^{31}P NMR spectrum of **6A/6B** shows two doublets at δ 130.5 ($^2J_{PP}$ = 37.8 Hz) and 128.3 ($^2J_{PP}$ = 25.6 Hz) and two doublets at δ 99.7 ($^2J_{PP}$ = 37.8 Hz) and 97.7 ($^2J_{PP}$ = 25.6 Hz) assigned to the coordinated [PhP(Cl)-*i*-PrN] and [PhP(*i*-PrNH)-*i*-PrN] phosphorus centers, respectively. In general, the ^{31}P NMR spectral resonances of molybdenum phosphine complexes shift to lower field relative to that of their phosphine precursors;[1,18–21] e.g., the ^{31}P NMR spectral resonances for *i*-PrN[PhP(*i*-PrNH)]$_2Mo(CO)_4$ is shifted 30.1 ppm relative to that of the free ligand *i*-PrN(PhP-*i*-$PrNH)_2$ (**1A**) (δ 90.2 vs 60.1).[1]

The structure of the **5A**-$Mo(CO)_4$ complex, **6A**, is confirmed by a single-crystal X-ray analysis. The structure is shown in Figure

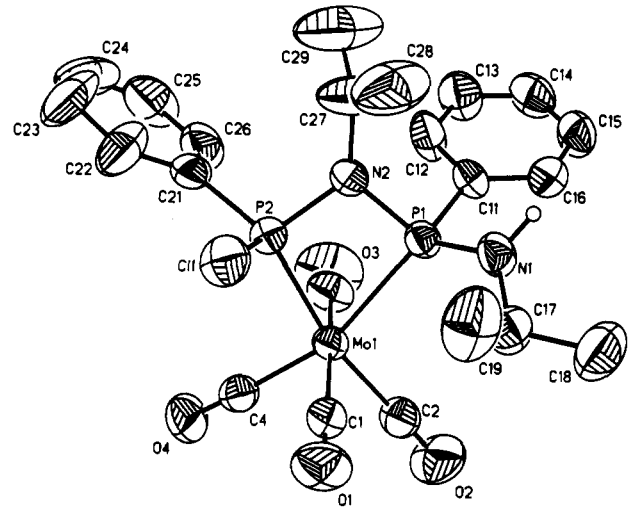


Figure 1. Structure and numbering scheme for *i*-PrN[PhPCl][PhP(*i*-PrNH)]$Mo(CO)_4$ (**6A**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table IV. Selected Structural Parameters for *i*-PrN[PhPCl][PhP(*i*-PrNH)]$Mo(CO)_4$ (**6A**)

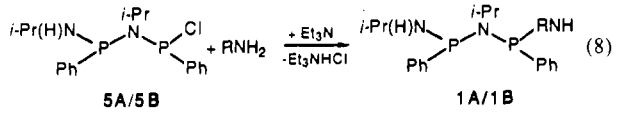
	(a) Bond Distances (Å)		
Mo(1)–P(1)	2.523 (1)	Mo(1)–P(2)	2.452 (1)
Mo(1)–C(2)	2.007 (5)	Mo(1)–C(1)	2.054 (5)
Mo(1)–C(3)	2.011 (5)	Mo(1)–C(4)	1.971 (5)
Cl(1)–P(2)	2.086 (2)	P(1)–N(1)	1.648 (4)
P(1)–N(2)	1.740 (4)	P(1)–C(11)	1.831 (4)
P(2)–N(2)	1.673 (3)	P(2)–C(21)	1.813 (5)
N(1)–C(17)	1.462 (6)	N(2)–C(27)	1.483 (7)
O(2)–C(2)	1.137 (7)	O(1)–C(1)	1.143 (6)
O(3)–C(3)	1.131 (7)	O(4)–C(4)	1.155 (6)
	(b) Bond Angles (deg)		
P(1)–Mo(1)–P(2)	64.7 (1)	P(1)–Mo(1)–C(2)	102.2 (1)
P(2)–Mo(1)–C(2)	166.2 (1)	P(1)–Mo(1)–C(1)	98.6 (1)
P(2)–Mo(1)–C(1)	89.8 (1)	C(2)–Mo(1)–C(1)	87.8 (2)
P(1)–Mo(1)–C(3)	89.3 (2)	P(2)–Mo(1)–C(3)	97.2 (1)
C(2)–Mo(1)–C(3)	86.6 (2)	C(1)–Mo(1)–C(3)	171.1 (2)
P(1)–Mo(1)–C(4)	161.9 (1)	P(2)–Mo(1)–C(4)	98.9 (1)
C(2)–Mo(1)–C(4)	94.6 (2)	C(1)–Mo(1)–C(4)	88.5 (2)
C(3)–Mo(1)–C(4)	85.1 (2)	Mo(1)–P(1)–N(1)	123.4 (1)
Mo(1)–P(1)–N(2)	93.8 (1)	N(1)–P(1)–N(2)	112.0 (2)
Mo(1)–P(1)–C(11)	122.2 (1)	N(1)–P(1)–C(11)	100.9 (2)
N(2)–P(1)–C(11)	102.6 (2)	Mo(1)–P(2)–Cl(1)	115.5 (1)
Mo(1)–P(2)–N(2)	98.1 (1)	Cl(1)–P(2)–N(2)	105.2 (1)
Mo(1)–P(2)–C(21)	129.5 (2)	Cl(1)–P(2)–C(21)	99.8 (2)
N(2)–P(2)–C(21)	106.3 (2)	P(1)–N(1)–C(17)	126.1 (3)
P(1)–N(2)–P(2)	102.6 (2)	P(1)–N(2)–C(27)	130.4 (3)
P(2)–N(2)–C(27)	125.8 (3)	Mo(1)–C(2)–O(2)	178.3 (5)
Mo(1)–C(1)–O(1)	176.4 (4)	Mo(1)–C(3)–O(3)	174.2 (5)
Mo(1)–C(4)–O(4)	176.1 (4)		

1. The complex consists of a molecule of **5A** cis-coordinated to the $Mo(CO)_4$ in a structure in an arrangement which has both Ph groups on one side and one Cl and one *i*-PrNH group on the opposite side of the Mo–P(1)–P(2)–N(2) ring. Thus, **6A** is the *erythro* ("meso-like") diastereomer.[22] The structural parameters (Table IV) indicate that it is similar to other known bis(phosphino)molybdenum complexes.[1,18–21] The mean Mo–P, P–N(terminal), and P–N(P–N–P bridge) distances of 2.488 (1), 1.648 (4), and 1.707 (4) Å are consistent with those observed in [*i*-PrN(PhP-*i*-$PrNH)_2$]$Mo(CO)_4$.[1] The MoP_2N ring is not planar or symmetrical; the dihedral angle between the Mo(1)–P(1)–P(2) and P(1)–P(2)–N(2) planes is 9.2° and the P(1)–N(2) + Mo(1)–P(1) distance of 4.26 Å is significantly greater than the P(1)–N(2) + Mo(1)–P(2) distance of 4.13 Å. The geometry around Mo is close to octahedral, but the CO ligands are bent slightly down from the large bis(phosphino)amine ligand. The

(17) Hart, W. A.; Sisler, H. H. *Inorg. Chem.* **1964**, *3*, 617.
(18) Tarassoli, A.; Chen, H.-J.; Thompson, M. L.; Allured, V. S.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1986**, *25*, 4152.
(19) King, R. B. *Acc. Chem. Res.* **1980**, *13*, 243.
(20) King, R. B.; Lee, T. W. *Inorg. Chem.* **1982**, *21*, 319 and references cited therein.
(21) McFarlane, W.; Bookham, J. L.; Colquhoun, I. J.; Thornton-Pett, M. *J. Organomet. Chem.* **1988**, *354*, 313.
(22) March, J. *Advanced Organic Chemistry*; 3rd ed.; Wiley Interscience: New York, 1985.

mean cis P–Mo–C angle is 96.0°. The P–N–P angle of 102.6° is smaller than the approximately 120° angle found in similar uncoordinated bis(phosphino)amines such as **12** (see below).

Our results show that **5A/5B** forms rapidly and is the intermediate whose subsequent amination is essential to the diastereomer selection process. This is verified in reactions between **5A/5B** and *i*-$PrNH_2/Et_3N$. Reactions were carried out by adding slight excesses of both amines to a solution of **5A/5B** (>80% **5A/5B**) as in eq 8. Reaction proceeds smoothly, converting all



5A/5B **1A/1B**

5A/5B to **1A/1B**, as observed by ^{31}P NMR spectral analysis. The *meso*:*d*,*l* diastereomer ratio was found typically to be 30–35:1 suggesting that **1A/1B** forms from **5A/5B** as in step g, Scheme I. Interestingly, when the reaction was repeated in the absence of Et_3N, the *meso*:*d*,*l* diastereomer ratio was typically lower, ca. 10:1. Although the role of Et_3N in the diastereoselection process is not understood, it might be that the amine simply aids in the rapid removal of the HCl group from the system in the form of the insoluble Et_3NHCl salt.

Because **5A/5B** is the key intermediate in the diastereoselective formation of **1A**, it was of interest to examine reactions of **5A/5B** with other primary amines to determine if reactions of the type shown in eq 8 are general and how the R group size might affect the reaction diastereoselectivity. Reactions of **5A/5B** with $MeNH_2$, $EtNH_2$, *t*-$BuNH_2$, and $PhNH_2$ in the presence of Et_3N were carried out under conditions analogous to those in the *i*-$PrNH_2/Et_3N$ reaction above, by adding the amines to the solutions containing **5A/5B**. Because of the high volatility of $EtNH_2$ and $MeNH_2$, these amines were transferred under vacuum to the reaction solutions of **5A/5B** and Et_3N at −78 °C. All reactions proceed cleanly to produce primarily the products *i*-PrN[PhP(*i*-PrNH)][PhP(RNH)] (**7A/7B**, R = Me; **9A/9B**, R = Et; **12**, R = *t*-Bu; **15**, R = Ph) with high diastereoselectivity. Typically **7A**:**7B** and **9A**:**9B** ratios were 6–12.4:1 and 15–23.5:1, respectively. We also observed minor amounts (<10%) of species tentatively characterized, from ^{31}P NMR data, as PhP(MeNH)-*i*-PrNH (**8**), PhP(*i*-PrNH)EtNH (**10**), and both diastereomers of *i*-PrN(PhPEtNH)$_2$ (**11A/11B**). **5A/5B** reactions with *t*-$BuNH_2/Et_3N$ and $PhNH_2/Et_3N$ produced only one isomer, **12** and **15**, respectively. Minor amounts (<10%) of tentatively characterized PhP(*t*-BuNH)-*i*-PrNH (**13**) and *i*-PrN[PhP(*t*-BuNH)]$_2$ (**14**) in the *t*-$BuNH_2/Et_3N$ reaction and PhP(*i*-PrNH)PhNH (**16**) in the $PhNH_2/Et_3N$ reaction were also observed; however, these were identified by their solution spectra only. Compounds **9A**, **12**, and **15** were obtained pure as crystalline solids.

Compounds **7A/7B**, **9A/9B**, **12**, and **15** were characterized by ^1H and ^{31}P NMR, mass (EI^+ and EI^+ exact mass), and IR spectral and elemental analysis data. Characterization of the **7A/7B** mixture is based only on ^{31}P NMR and mass spectral (EI^+ and EI^+ exact mass) data which were in good agreement with those for the other members of the series. All the unsymmetrical bis(phosphino)amines give mass spectral parent molecular ions. From X-ray structural analysis of selected series members and by ^{31}P NMR spectral correlation, bis(phosphino)amine structures are established for the entire series.

The structure of **12** (Figure 2) and its absolute configuration were determined by single-crystal X-ray analysis. Because **12** formed monodiastereomerically, there was the possibility that it may have been produced in a different isomeric form from the other products in the series; however, we determined that it too is the *erythro* diastereomer.[22] The structural parameters (Table V), bond lengths and angles, are similar to those of other known bis(phosphino)amines,[23-25] except for the P(1)–N(2)–P(2) angle

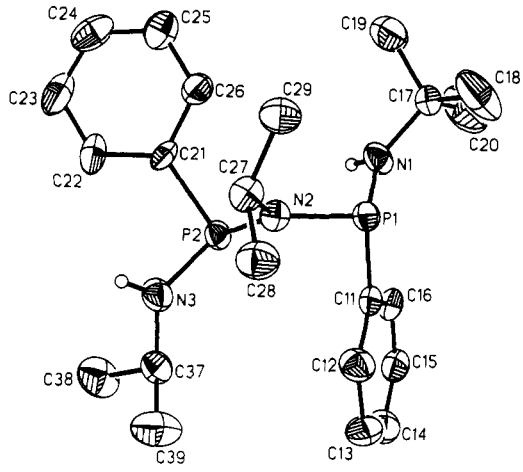


Figure 2. Structure and numbering scheme for *i*-PrN[PhP(*t*-BuNH)][PhP(*i*-PrNH)] (**12**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table V. Selected Structural Parameters for *i*-PrN[PhP(*t*-BuNH)][PhP(*i*-PrNH)] (**12**)

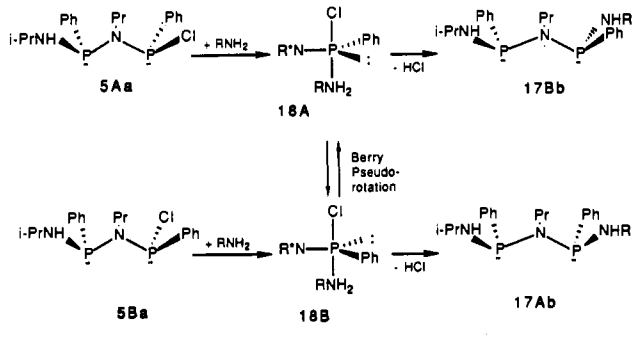
(a) Bond Lengths (Å)			
P(1)–N(1)	1.668 (4)	P(1)–N(2)	1.721 (3)
P(1)–C(11)	1.840 (4)	P(2)–N(2)	1.710 (3)
P(2)–N(3)	1.673 (4)	P(2)–C(21)	1.843 (4)
N(1)–C(17)	1.472 (5)	N(2)–C(27)	1.492 (5)
N(3)–C(37)	1.461 (5)		
(b) Bond Angles (deg)			
N(1)–P(1)–N(2)	106.9 (2)	N(1)–P(1)–C(11)	102.2 (2)
N(2)–P(1)–C(11)	99.2 (2)	N(2)–P(2)–N(3)	108.5 (2)
N(2)–P(2)–C(21)	100.7 (2)	N(3)–P(2)–C(21)	100.3 (2)
P(1)–N(1)–C(17)	127.7 (3)	P(1)–N(2)–P(2)	120.4 (2)
P(1)–N(2)–C(27)	118.2 (2)	P(2)–N(2)–C(27)	121.3 (2)
P(2)–N(3)–C(37)	123.5 (3)		

of 120.4° which is larger than those observed for the majority of the other known bis(phosphino)amines (109°).[26] The phosphorus lone-pair electron vectors are approximated by perpendiculars to the N(1)–N(2)–C(11) plane and the N(3)–N(2)–C(21) plane through the P atoms. The dihedral angles between these vectors and the P(1)–N(2)–P(2) plane of the molecule are 79.7° at P(1) and −91.1° at P(2). Thus, the lone pair electrons are approximately orthogonal to the planar N(2) lone-pair electrons. In addition, the phosphorus lone pairs are rotated ca. 180° from each other, producing a trans arrangement around the P–N–P skeleton. Since the structures of *i*-PrN[(PhP-*i*-PrNH)]$_2$ (**1A**), the major diastereomer of **1**, and **12** are both *meso* and *erythro* ("meso-like") diastereomers and their solution spectra closely correlate with those of the major diastereomer in **7A/7B** and with **15**, we conclude that the major diastereomers **7A**, **9A**, and **15** are all also *erythro* diastereomers.

Comparison of the conformational properties of **12** to those of other known bis(phosphino)amines $RN(PXX')_2$ (R = alkyl, phenyl; X, X' = alkoxy, amino, halogen, phenyl) is of interest, but difficult because limited structural work has been reported on other bis(phosphino)amines.[23-27] In general, the $RN(PXX')_2$ compounds assume a conformation around their P–N–P skeleton in which the phosphorus lone-pair electrons are cis-oriented, similar to what occurs in the structures of bis(phosphino)amines coordinated to $Mo(CO)_4$ fragments. In only one case, the bis(phosphino)amine *i*-$PrN(PPh_2)_2$, was a similar trans conformation confirmed.[24] Although several factors may contribute to conformation selection in a given $RN(PXX')_2$ system, it should be noted that in cases where a trans conformation is seen, the com-

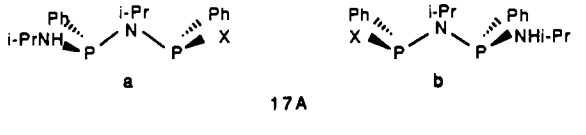
(23) Chen, H.-J.; Barendt, J. M.; Haltiwanger, R. C.; Hill, T. G.; Norman, A. D. *Phosphorus Sulfur* **1986**, *26*, 155.
(24) Keat, R.; Manojlovic-Muir, L.; Muir, K. W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2192.
(25) Thompson, M. L.; Tarassoli, A.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1987**, *26*, 684.
(26) Cross, R. J.; Green, T. H.; Keat, R. *J. Chem. Soc., Dalton Trans.* **1976**, 1424.
(27) Nöth, H.; Fluck, E. *Z. Naturforsch., B* **1984**, *39B*, 744.

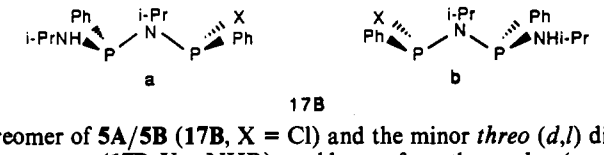
Scheme II



pounds have the bulky isopropyl group on the central nitrogen of the compound. Thus, it is possible that a sterically demanding group at the central nitrogen may in effect control the skeletal conformation.[24]

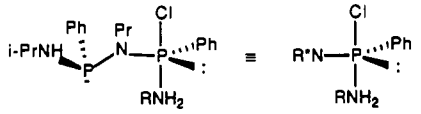
The intermediate isolation and reactivity studies described above suggest that i-$PrNH_2/PhPCl_2/Et_3N$ react to form **1A/1B** in a series of four steps; (i and ii) initially **2** and **3** are formed stepwise, (iii) **3** and $PhPCl_2$ react to form the bis(phosphino)amine **5A/5B** (step d), and finally (iv) **5A/5B** is aminated (step g) to **1A/1B**. Although alternate pathways may participate, such as one which involves **4A/4B**, these appear to be minor contributors. Perhaps the most significant feature of this mechanism is that diastereomer selection occurs not at the stage where the bis(phosphino)amine P–N–P skeleton is formed, i.e. in the **3**/$PhPCl_2$ reaction to **5A/5B**, but in a process which involves amination of a terminal P–Cl bond. A similar situation may occur in the formation of $MeN[P(Cl)NMe_2]_2$ from the $MeN(PCl_2)_2/Me_3SiNMe_2$ reaction, a reaction which is reported[3] but not yet confirmed to give the product monodiastereomerically. Although we cannot state conclusively how the **5A/5B** mixture is aminated diastereoselectively to the *erythro* (or *meso*, **1A**) diastereomer products, several observations can be made. Since we see no evidence for the presence of cyclic intermediates, perhaps of the diazadiphosphetidine type,[7-11] between **5A/5B** and the final products **1A/1B**, **7A/7B**, **9A/9B**, **12**, and **15** and because cyclic products did not form from reactions of **5A/5B** with Et_3N, we conclude that the diastereoselection process involves only acyclic species. Further, we assume that, like their P(V) analogues,[28] reactions of phosphorus(III) chlorides with amines occur via an S_N2 process in which inversion of configuration at the phosphorus center follows displacement of the chloride group. Thus, if no configurational change occurs at the remote phosphorus during reaction of the RNH_2 amine with **5A/5B**,[29] the major *erythro* (*meso*) diastereomer products (**17A**, X = NHR) would form by amination of the *threo* (*d,l*) diaste-





reomer of **5A/5B** (**17B**, X = Cl) and the minor *threo* (*d,l*) diastereomers (**17B**, X = NHR) would come from the *erythro* (*meso*) diastereomer (**17A**, X = Cl).[30] Thus, the question becomes by what process does the essentially 1:1 *threo* (*d,l*)/*erythro* (*meso*) **5A/5B** mixture undergo conversion to the predominantly *erythro* (*meso*) product?

A reasonable route by which the diastereo selection could occur is shown in Scheme II, a process in which enantiomer interconversion occurs through participation of a five-coordinate intermediate.[31-33] Such an intermediate (**18**) could undergo intra-



molecular exchange via Berry pseudorotation[34] to a thermodynamically favored, pre-*erythro* product before elimination of the chloride ion. In the scheme, the reactions and interrelationships of one enantiomer (e.g. **a**) from each diastereomer type (**5Aa** and **5Ba**) is shown. Through attack of RNH_2 at phosphorus, the five-coordinate intermediates **18A** and **18B** could form. Following valence-shell electron pair repulsion (VSEPR)[35] rules and known stereochemical principles in five-coordinate species,[36] we might expect the phosphorus lone-pair electrons, the phenyl group, and the bulky phosphinoamine (R*) group to occupy the equatorial positions.[31,36] The RNH_2 and the electronegative Cl leaving group would be in axial positions. Without intermediate interconversion, *erythro*-**5A** forms *threo*-**17B** and *threo*-**5B** forms *erythro*-**17A**. However, if rearrangement of **18A** to **18B** occurs, because **18B** is more stable, the originally 1:1 **5A/5B** mixture could aminate to mainly *erythro* products. This mechanism requires that the intermediate species **18A** and **18B** can pseudorotate to the lowest energy conformer in a process which depends on specific steric and yet to be defined interactions between the five-coordinate phosphorus site and the R*N unit of the intermediate.[36] The reactions of RNH_2 with **5A/5B** show a steric dependence on the R group size. The degree of stereoselection increases as the R group size increases in the series $MeNH_2$ to t-$BuNH_2$. This result seems consistent with the mechanism in Scheme II, since the RNH_2 amine in the axial position occupies a sterically encumbered position, which could be increasingly less desirable in one enantiomeric intermediate form than the other.

The mechanism by which diastereoselection occurs, the generality of the reaction, and extent to which it can be applied to other diastereomer bis(phosphino)amine syntheses remain to be determined. We are presently examining these systems further and will report more on them later.

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Supplementary Material Available: Tables of crystal data and refinement details, anisotropic displacement parameters, hydrogen atom coordinates, bond distances and angles, and least-squares planes and dihedral angles (16 pages); tables of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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