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Diastereomeric Selective Formation of a Linear Diphosphazane: *meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$

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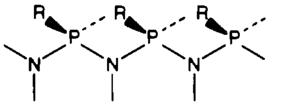
Reaction of $PhPCl_2$ with *i*-$PrNH_2$ and Et_3N yields a 9–12:1 *meso*:*d*,*l* mixture of *i*-PrN[PhP(*i*-PrNH)]$_2$ (**6**). *meso*-**6** has been characterized by spectral (IR, MS, and ^1H and ^{31}P NMR) data and as the *cis*-*meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$Mo(CO)$_4$ (**14**) complex by X-ray structural analysis: triclinic, $P\bar{1}$, $a = 16.928$ (6) Å, $b = 19.118$ (6) Å, $c = 10.215$ (3) Å, $\alpha = 97.52$ (3)°, $\beta = 96.78$ (3)°, $\gamma = 80.10$ (3)°, $V = 3213$ (2) Å^3, $Z = 4$, $R = 0.064$, $R_w = 0.074$. Reaction of $PhPCl_2$ with $PhNH_2$ and Et_3N yields a 1:1 mixture of *meso*- and *d*,*l*-PhN[PhP(PhNH)]$_2$ (**13**). $MeNH_2$, $EtNH_2$, and *t*-$BuNH_2$ reactions with $PhPCl_2$ proceed without evidence for formation of analogues of **6**. The $PhPCl_2$/*i*-$PrNH_2$ reactions have been examined as a function of temperature and reactant ratio. At low *i*-$PrNH_2$:$PhPCl_2$ ratios (1.0:0.5) the intermediate PhP(Cl)NH-*i*-Pr (**7**) is observed and has been characterized by X-ray analysis as the complex *cis*-[PhP(Cl)NH-*i*-Pr]$_2$Mo(CO)$_4$ (**15B**): triclinic, $P\bar{1}$, $a = 8.2734$ (16) Å, $b = 11.0633$ (26) Å, $c = 15.3991$ (35) Å, $\alpha = 93.296$ (19)°, $\beta = 98.572$ (17)°, $\gamma = 91.827$ (17)°, $V = 1390.3$ Å^3, $Z = 2$, $R = 0.039$, $R_w = 0.036$. The role of partially aminated intermediates in the diastereomer selection process and the sequence of reactions by which *meso*-**6** forms are discussed.

Introduction

The synthesis of oligomeric/polymeric phosph(III)azanes,[1-3] and the subsequent investigation of their properties, raises questions about how such systems might be obtained in stereoregular[4] isotactic (**1**) or syndiotactic (**2**) forms. These could have structural, physical, and chemical properties significantly different from each other and from randomly formed atactic compounds.[4,5] Interestingly, stereoregular polymerization in inorganic condensation polymerization processes appears largely undocumented[4,6-8] and could constitute a future area of challenge in inorganic polymer synthesis.



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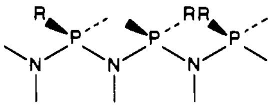

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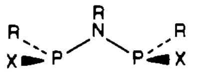
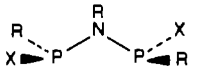
To develop routes to stereoregular linear polyphosph(III)azanes, it is necessary to examine reactions by which P–N–P bond units are formed. Since unsymmetrically substituted bis(phosphino)amines (3) are the minimal-sized units needed to define a stereoregular linear system, reactions by which they arise become important. Although several routes to phosphorus(III) bis(phosphino)amines are known,[9-12] only fragmentary reports of chiral-phosphorus-containing bis(phosphino)amines have appeared.[12-15] Prior to our work, only MeN[P(Cl)NMe$_2$]$_2$,[15] MeN(ClPBr)$_2$,[15] and MeN[P(Cl)Me]$_2$[14b,15] had been reported as single diastereomers; however, their characterization depended alone on ^{31}P NMR spectral data. Only when we reported in preliminary form the diastereomerically selective formation of *meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$ (**3A**; R = Ph, X = *i*-PrNH)[16] was unambiguous evidence shown for diastereoselective bis(phosphino)amine formation. This work is now reported in detail below.



3A (*meso*)



3B (*d*, *l*)

Experimental Section

Apparatus and Materials. All operations were carried out in N_2-flushed glovebags and standard vacuum-line equipment.[17] Infrared, ^1H NMR (90.0 MHz), and mass spectra were obtained by using Beckman IR4250 or IBM FTIR (IR/32 Type 9132), JEOL FX 90Q, and Varian MAT CH5 or V.G. Analytical 7070 EQ-HF spectrometers, respectively. ^{31}P NMR spectra were obtained on the FX-90Q (36.4 MHz) spectrometer. ^1H and ^{31}P NMR chemical shifts (+δ = downfield shift) were measured relative to internal Me_4Si and external 85% H_3PO_4, respectively. In cases where relative spectral areas in ^{31}P NMR spectra were critical (e.g. **6A**:**6B**:**5**, below), the areas measured in decoupled [$^{31}P\{^1H\}$] spectra were compared with those measured in undecoupled [^{31}P] experiments. In all cases, area agreement was within ±20%.

PhN(PCl$_2$)$_2$,[10c] PhP(PhNH)$_2$ (**4**),[25] PhP(*i*-PrNH)$_2$ (**5**),[16,18] and (nor)Mo(CO)$_4$[19] (nor = norbornadiene) were prepared as described previously. Me_2NH, Et_2NH, $EtNH_2$, and $MeNH_2$ (Matheson Gas Products) were passed over BaO before use. PCl_3 (Strem Chemicals), $PhPCl_2$ (Strem Chemicals), $PhNH_2$ (J. T. Baker Chemical), *t*-$BuNH_2$ (Aldrich Chemical), *i*-$PrNH_2$ (Aldrich), and Et_3N (Baker Chemical) were distilled from CaH_2 immediately before use. Toluene (Fisher Scientific) was distilled from Na–Pb alloy. Et_2O (Mallinckrodt, anhydrous) was used as obtained.

Reactions of $PhPCl_2$. (A) With *i*-$PrNH_2$. PhP(*i*-PrNH)$_2$ (5) and *i*-PrN[PhP(*i*-PrNH)]$_2$ (6). *i*-$PrNH_2$ (165 mmol) and Et_3N (166 mmol)

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were added dropwise to a toluene solution (250 mL) of $PhPCl_2$ (73.7 mmol) at 0 °C. After 15 h at 25 °C, Et_3NHCl was removed by filtration and the filtrate volume was reduced in vacuo. The $^{31}P\{^1H\}$ NMR spectrum of the filtrate exhibited singlet resonances at δ 60.2, 59.1, and 57.8 (relative areas of 9–12:1:8–10). Crystallization from the toluene solution at −15 °C yields initially *meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$ (*meso*-**6**) (δ 60.2), a mixture of *meso*- and *d,l*-*i*-PrN[PhP(*i*-PrNH)]$_2$ (*meso*-**6** and *d,l*-**6**), and finally PhP(*i*-PrNH)$_2$ (**5**) (δ 57.8). Repeated crystallization from toluene yields pure *meso*-**6**. Anal. Calcd for $C_{21}H_{33}P_2N_3$: C, 64.76; H, 8.54; N, 10.79; P, 15.91. Found: C, 64.22; H, 8.59; N, 10.59; P, 15.91. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 60.2 (s). ^1H NMR ($CDCl_3$): δ 1.23 (J = 6.9 Hz, area 18; CH_3), 2.31 (s, broad, area 2; NH), 3.41 (m, area 3; CH), 7.22 (m, area 10; C_6H_5). MS: M^+, *m/e* 389 [$C_{21}H_{33}P_2N_3^+$]. IR (KBr, cm^{-1}) characteristic ν: 3337 (w, NH), 1380 (m), 1361 (m), 1168 (vs), 1126 (vs), 868 (s), and 853 (s).

After complete precipitation of **6**, the solution containing **5** was evaporated to dryness, and **5** was recrystallized from toluene. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.8 (s). ^1H NMR ($CDCl_3$): δ 1.12 (d of d, J = 6.6 Hz, area 12; CH_3), 1.94 (broad d, J = 8.9 Hz, area 2; NH), 3.24 (m, area 2; CH), 7.36 (m, area 5; C_6H_5). MS and IR spectral and elemental analytical data were published previously.[18]

i-$PrNH_2$ (162 mmol) in 100 mL of toluene was added dropwise to $PhPCl_2$ (37 mmol) in toluene at 0 °C. No Et_3N was present. ^{31}P NMR spectral analysis of the reaction mixture showed resonances at δ 60.2 (s), 59.1 (s), and 57.8 (s) (areas 10:1.0:200).

Reactions of *i*-$PrNH_2$ with $PhPCl_2$ in the presence of Et_3N were carried out at *i*-$PrNH_2$:$PhPCl_2$:Et_3N mole ratios of 24:1:15, 2.2:1:2.7, 1:1:1, and 2.0:1.0:1.0. At the higher amine:$PhPCl_2$ ratios, the relative mole ratios of *meso*-**6**:*d,l*-**6**:**5**, as determined by ^{31}P NMR spectral analysis, were 14:1:38 and 8:1:6. At the lower ratios, evidence was obtained for reaction intermediates. At the 1:1:1 reactant ratio singlet resonances at δ 160 (area 2; $PhPCl_2$), 121.1 [area 12; PhP(Cl)-*i*-PrNH (**7**)], 124 (area 1; **8**), and broad resonance pairs at δ 128 and 68 and δ 126 and 65 (area 4; **9**) were observed. From the 2:1:1 reactant ratio, only resonances at δ 160 ($PhPCl_2$) and 121.1 (**7**) (ratio 1:1) appear. Attempts to isolate products from these mixtures by crystallization or thin-layer chromatography were unsuccessful; however, **7** was isolated as the Mo(CO)$_4$ complex (see below).

i-$PrNH_2$ (165 mmol)/Et_3N (166 mmol) mixtures were combined with $PhPCl_2$ (74 mmol) in toluene (250 mL), in separate experiments, at −78, 0, +25, and +110 °C. After reactant combination was complete, reactions were returned to room temperature. ^{31}P NMR spectral analysis of the reaction mixtures showed *meso*-**6**:*d,l*-**6**:**5** product mole ratios of 10:1:16 (−78 °C), 8:1:20 (0 °C), 11:1:29 (+25 °C), and 2.3:1:1 (+110 °C).

(B) With *t*-BuNH$_2$. *t*-$BuNH_2$ (0.11 mol) and Et_3N (0.15 mol) in toluene were added dropwise under N_2 to $PhPCl_2$ (0.074 mol) in toluene at 0 °C. After 15 h at 25 °C, Et_3NHCl was filtered and the filtrate reduced in vacuo to one-third of the original volume. The filtrate showed ^{31}P NMR resonances at δ 116.5 [area 5; PhP(Cl)-*t*-BuNH (**10**)], 155.6 (area 1; **11**), and 41.4 [area 3; PhP(NH-*t*-Bu)$_2$ (**12**)]. Crystallization from toluene yielded mixtures of **10** and **12**. Pure samples of **10** were not obtained.

Excess *t*-$BuNH_2$ and Et_3N were added to the above filtrate solution at 0 °C. ^{31}P NMR spectral analysis of the resulting mixture showed resonances due to **10** and **12** only (areas 15:1).

(C) With MeNH$_2$ or EtNH$_2$. $MeNH_2$ or $EtNH_2$ (92 mmol) was condensed at −196 °C onto $PhPCl_2$ (37 mmol) and Et_3N (111 mmol) in toluene (50 mL). The mixtures were warmed to −78 °C and then slowly to +25 °C. ^{31}P NMR resonances appeared as follows: for $MeNH_2$, δ 69.7 (s), a collection of unassigned minor peaks at δ 80–110, and minor oxidation product peaks at δ 21.8 and 14.4; for $EtNH_2$, a major resonance at δ 64.6 and minor unassigned resonances at δ 78–92.

(D) With PhNH$_2$. PhP(PhNH)$_2$ (4) and PhN[PhP(NHPh)]$_2$ (13). $PhNH_2$ (0.17 mol) and Et_3N (0.17 mol) were added dropwise to $PhPCl_2$ (0.074 mol) in toluene at 0 °C under N_2. After 15 h at 25 °C, Et_3NHCl was filtered and the filtrate volume was reduced. The ^{31}P NMR spectrum of the filtrate showed resonances at δ 62.2 and 61.0 (area 1:1; **13A** and **13B**) and 45.3 (area 3; **4**). **4** crystallized from the toluene solution. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 45.2 (s). ^1H NMR ($CDCl_3$): δ 4.78 (s, area 2; NH), 7.20 (m, area 15; C_6H_5). MS and IR spectral and elemental analytical data were reported previously.[20]

Evaporation of toluene in vacuo from the above reaction solution, extraction of the residue with Et_2O, and recrystallization from pentane yielded >90% isomer pure diastereomer **13A**. Anal. Calcd for $C_{30}H_{27}P_2N_3$: C, 73.30; H, 5.54; N, 8.55; P, 12.61. Found: C, 73.41; H, 5.50. MS, M^+, *m/e* 491 [$C_{30}H_{27}P_2N_3^+$]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.0 (s). ^1H NMR (C_6D_6): δ 6.4–8.1 (m; C_6H_5). Diastereomer **13B** could not be obtained free of **13A** and **4**; hence, it was not characterized further.

Table I. Crystallographic Data for *i*-PrN[PhP(*i*-PrH)]$_2$Mo(CO)$_4\cdot{}^1/_2C_7H_8$ (**14**$\cdot{}^1/_2C_7H_8$) and {PhP(Cl)*i*-PrNH}$_2$Mo(CO)$_4$ (**15B**)

	14$\cdot{}^1/_2C_7H_8$	**15B**
formula	$MoP_2O_4N_3C_{25}H_{33}\cdot{}^1/_2C_7H_8$	$MoP_2O_4N_2Cl_2C_{22}H_{26}$
fw	643.53	611.98
space group	$P\bar{1}$	$P\bar{1}$
a, Å	16.928 (6)	8.2734 (16)
b, Å	19.118 (6)	11.0633 (23)
c, Å	10.215 (3)	15.3991 (35)
α, deg	97.52 (3)	93.296 (19)
β, deg	96.78 (3)	98.572 (17)
γ, deg	80.10 (3)	91.827 (17)
V, Å^3	3213 (2)	1390.3 (5)
d_c, g cm^{-3}	1.33	1.462
Z	4	2
$F(000)$	1332	620
μ, cm^{-1}	5.33	3.5
radiation; λ Å	Mo Kα, λ = 0.71073	Mo $K\alpha$; λ = .71073
T, °C	22–24	22–24
abs corr	none	empirical
transm factors	none	0.850, 0.802
R	0.0645	0.028
R_w	0.0739	0.036

Reaction of PhN(PCl$_2$)$_2$ with Me$_2$NH. Me_2NH (22.5 mmol) in a toluene solution of $PhN(PCl_2)_2$ (24.0 mmol) and Et_3N (50.4 mmol) were warmed slowly from −196 to +25 °C. Reaction began below 0 °C. After 12 h, Et_3NHCl was filtered. The reaction mixture exhibited ^{31}P NMR resonances at δ 199.6 [$(ClPNPh)_2$[10c]], 164.9 (s), [Cl_2PNMe_2[21]], 155.4 (s) [$PhN(PCl_2)_2$[10c]], and two minor coupled doublets at δ 152.2 and 133.7 (J = 70.8 Hz). Attempts to isolate the doublet-producing products were unsuccessful.

***i*-PrN[PhP(*i*-PrNH)]$_2$Mo(CO)$_4$ (14).** To (nor)Mo(CO)$_4$ (1.5 mmol) in toluene was added *meso*-**6** (1.1 mmol) in toluene dropwise at room temperature under N_2. After 15 h at 25 °C, the solution was filtered, and solvent was removed in vacuo. ^{31}P NMR spectral analysis of the filtrate showed only a singlet resonance at δ 90.3 due to **14**. Recrystallization of the product from toluene yielded pure **14** (mp 181–184 °C; yield >90%). Anal. Calcd for $MoP_2N_3O_4C_{25}H_{33}$: C, 50.26; H, 5.57; N, 7.03; P, 10.37. Found: C, 51.28; H, 5.84; N, 7.22; P, 10.58. $^{31}P\{^1H\}$ NMR (C_6D_6, at 36.4 or 101 MHz): δ 90.3 (s). ^1H NMR ($CDCl_3$): δ 1.14 (d, J = 6.6 Hz, area 3; CH_3), 1.45 (d of d, J = 6.6 Hz, J = 2.0 Hz, area 12; CH_3), 2.19 (d, J = 10.0 Hz, area 2, NH), 3.62 (m, area 3; CH), 7.41 (m, area 10; C_6H_5). MS: M^+, *m/e* 589 [$^{98}MoP_2N_3O_4C_{25}H_{33}^+$]. IR (KBr, cm^{-1}): characteristic ν at 3370 (w), 2973 (m), 2933 (w), 2013 (vs), 1913 (vs), 1893 (vs), 1871 (vs) 881 (m).

***cis*-[PhP(Cl)-*i*-PrNH]$_2$Mo(CO)$_4$ (15A,B).** To a solution that contained $PhPCl_2$ (11.1 mmol) and PhP(Cl)NH-*i*-Pr (**7**) (22.2 mmol) prepared from a 1.0:0.5 *i*-$PrNH_2$:$PhPCl_2$ reaction, a slight excess of (nor)Mo(CO)$_4$ in toluene was added dropwise at 0 °C. After 12 h, the reaction solution exhibited two equal-area ^{31}P NMR spectral resonances at δ 142.7 (**15A**) and 145.3 (**15B**) (90% yield). The mixture was filtered, passed through a 2-cm alumina column, reduced to 1/10 volume, and cooled to −15 °C. **15B** crystallized first from solution. **15A** was not obtained free of **15B**, although mass and ^{31}P NMR spectral data showed clearly that **15A** and **15B** are isomers. Recrystallization of **15B** from toluene yielded pure product (mp 139–141 °C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 145.3 (s). ^1H NMR ($CDCl_3$): δ 0.90 (d of d, J = 22.8 Hz, J = 6.4 Hz, area 12; CH_3); 3.1 (br, area 2; NH), 4.0 (br m, area 2; CH) 7.9 (m, area 10; C_6H_5) MS: M^+, EI^+, *m/e* 611 [$^{98}MoP_2N_2O_4C_{23}Cl_2H_{28}^+$]; CI^+, *m/e* 612. IR (KBr, cm^{-1}): characteristic ν at 2040 (vs), 1957 (vs), 1909 (vs) 1890 (sh).

Thermolyses. (A) PhP(*i*-PrNH)$_2$ (5). **5** was heated at 130 °C. *i*-$PrNH_2$ (identified by ^1H NMR) was removed continuously in vacuo as reaction proceeded. After 4 days, the reaction mixture consisted of an approximately equal molar mixture of *meso*-**6**, *d,l*-**6**, and unreacted **5**. Similar results were obtained for reactions carried out in sealed tubes, except typically the *meso*-**6** and *d,l*-**6** yields were lower.

(B) PhP(*t*-BuNH)$_2$ (12). **12** (neat) was heated at 130–180 °C for 10 days. No reaction occurred.

(C) **PhP(PhNH)$_2$ (4).** **4** at 130–140 °C for 4.5 days under continuous vacuum yielded an approximately equimolar mixture of diastereomer **13A** and **13B** (δ 62.2 and 61.1) and unreacted **4**.

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for i-PrN[PhP(i-PrNH)]$_2$Mo(CO)$_4$·$^1/_2$C$_7$H$_8$ (**14**·$^1/_2$C$_7$H$_8$)

	x	y	z	U_{eq}[a]
		(a) Molecule I		
Mo(1)	6857 (1)	2851 (1)	8030 (2)	44 (1)
P(1)	7514 (3)	1989 (2)	9629 (5)	46 (2)
P(2)	7776 (3)	3353 (2)	9866 (5)	42 (2)
O(1)	5941 (10)	1813 (9)	6026 (20)	138 (10)
O(2)	5172 (8)	3448 (8)	9176 (16)	93 (7)
O(3)	6445 (10)	4191 (9)	6463 (17)	110 (8)
O(4)	8308 (9)	2462 (9)	6250 (16)	97 (8)
C(1)	6255 (13)	2219 (12)	6752 (20)	79 (9)
C(2)	5800 (12)	3228 (10)	8833 (20)	65 (8)
C(3)	6564 (12)	3698 (11)	7013 (22)	68 (9)
C(4)	7785 (12)	2573 (11)	6904 (21)	68 (9)
N(1)	6992 (8)	1626 (7)	10583 (15)	59 (6)
N(2)	8097 (7)	2564 (6)	10523 (11)	40 (5)
N(3)	7503 (8)	4011 (6)	11036 (13)	51 (5)
C(17)	6151 (10)	1806 (10)	10741 (22)	67 (9)
C(18)	5968 (16)	1947 (17)	12081 (28)	184 (21)
C(19)	5715 (14)	1280 (16)	10031 (32)	196 (22)
C(27)	8627 (11)	2535 (10)	11805 (17)	64 (8)
C(28)	8104 (13)	2581 (11)	12979 (19)	91 (10)
C(29)	9270 (11)	1889 (11)	11809 (20)	95 (10)
C(37)	6683 (12)	4297 (11)	11325 (20)	73 (9)
C(38)	6629 (14)	4534 (14)	12768 (22)	129 (14)
C(39)	6332 (15)	4886 (14)	10548 (30)	163 (18)
		(b) Molecule II		
Mo(1′)	2113 (1)	2863 (1)	1947 (2)	41 (1)
P(1′)	2332 (3)	2206 (2)	3967 (5)	45 (2)
P(2′)	2639 (3)	3551 (2)	4025 (5)	46 (2)
O(1′)	1251 (10)	1772 (8)	−43 (15)	98 (8)
O(2′)	3739 (8)	2255 (8)	637 (15)	98 (7)
O(3′)	2023 (9)	3952 (7)	−109 (15)	84 (7)
O(4′)	333 (8)	3612 (8)	2487 (14)	90 (7)
C(1′)	1567 (10)	2161 (10)	699 (20)	60 (8)
C(2′)	3167 (11)	2454 (11)	1170 (18)	61 (8)
C(3′)	2047 (11)	3564 (10)	668 (19)	55 (8)
C(4′)	978 (12)	3335 (10)	2336 (18)	61 (8)
N(1′)	2989 (8)	1470 (7)	4144 (13)	54 (6)
N(2′)	2628 (7)	2910 (6)	5023 (12)	38 (5)
N(3′)	3515 (8)	3850 (7)	4259 (14)	55 (6)
C(17′)	3694 (14)	1238 (10)	3367 (21)	75 (9)
C(18′)	3499 (14)	697 (15)	2288 (31)	173 (18)
C(19′)	4437 (13)	967 (14)	4147 (27)	146 (16)
C(27′)	2950 (13)	2930 (11)	6419 (20)	71 (9)
C(28′)	3815 (14)	2571 (13)	6630 (21)	117 (13)
C(29′)	2472 (13)	2651 (12)	7301 (19)	95 (11)
C(37′)	4212 (10)	3564 (11)	3543 (19)	66 (8)
C(38′)	4969 (11)	3658 (13)	4452 (25)	119 (13)
C(39′)	4204 (12)	3913 (12)	2313 (22)	95 (11)

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

X-ray Analyses. (A) *meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$Mo(CO)$_4$ (14). Crystals of **14**, grown from toluene as clear parallelpipeds, tended to twin. Of three crytals mounted and examined for data collection, only one fragment of a larger crystal was suitable for data collection. All three gave the same unit cell. A summary of crystal data and details of the data collection and structure refinement are given in Table I. Positional parameters are given in Table II.

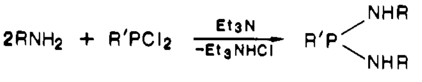
There are two independent molecules of **14** per asymmetric unit.[22] Because of concerns about crystal quality and whether we in fact had isolated a single crystal, we collected data using the faster Wycoff scan techniques as programmed by Nicolet.[23] Since **14** had a disordered toluene and the crystals were only marginally stable, θ–2θ data collection was not pursued.

In the final refinement, all phenyl rings were refined as rigid groups with the disordered toluene in three partially occupied positions. All atoms except the fixed phenyl carbons and the hydrogen atoms were refined with anisotropic temperature factors. All hydrogens were constrained to idealized, fixed geometries at the atom to which they were attached.

(B) *cis*-*d*,*l*-[PhP(Cl)NH-*i*-Pr]$_2$Mo(CO)$_4$ (15B). **15B** crystallizes from toluene as colorless plates. Crystals were coated in epoxy resin and mounted on a glass fiber. For the final refinement cycles, all non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogens had independent isotropic thermal parameters. Hydrogen atoms attached to nitrogen were refined with no constraints. Methyl group hydrogens were geometrically constrained and idealized but were allowed to rotate about the C–C bond as rigid groups. Other hydrogens were constrained to idealized geometries at their atom of attachment. Neutral scattering factors were used for all atoms of both **14** and **15B**.[24] Nicolet SHELXTL-PLUS programs were used, run on a Micro-VAXII system.[25]

Results and Discussion

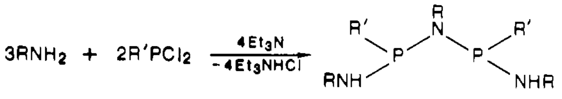
Reactions of primary amines (RNH$_2$; R = Me, Et, i-Pr, t-Bu, and Ph) with PhPCl$_2$ were examined as routes to chiral phosphorus containing bis(phosphino)amines. Earlier work had shown that primary amines react with alkyl- or aryldichlorophosphines (R′PCl$_2$) in the presence of an HCl scavenger, either excess primary amine or added tertiary amine, to form bis(amino)phosphines (**16**) (eq 1)[18,20] and, when cyclophosphazane formation



$$2RNH_2 + R'PCl_2 \xrightarrow[-Et_3NHCl]{Et_3N} R'P(NHR)_2 \qquad (1)$$

16

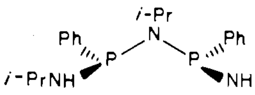
can be prevented,[9,26-30] bis(phosphino)amines (**17**) (eq 2).[16,25]



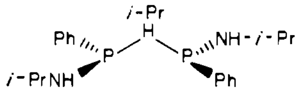
17

Since the latter reaction yields products containing chiral phosphorus atoms, it is a system in which to examine diastereoselective formation of bis(phosphino)amines.

i-PrNH$_2$ and PhPCl$_2$ in ratios greater than 1.5:1.0 react, in the presence of excess Et$_3$N, to yield i-PrN[PhP(i-PrNH)]$_2$ (**6**) along with PhP(i-PrNH)$_2$ (**5**).[18] Reaction occurs smoothly between 0 and 25 °C, according to eq 1 and 2 (R = i-Pr; R′ = Ph). ^{31}P NMR spectral analyses of reaction mixtures show that **5** and **6** are the only products. Compound **6** is a mixture of diastereomers, **6A** and **6B** (9–12:1), which exhibit ^{31}P NMR resonances at δ 60.2 and 59.1, respectively. Isomer **6A** is formed preferentially, indicating that the reaction is significantly diastereomerically selective. Compounds **6A** and **5** were isolated from reaction mixtures by fractional crystallization. **6A** crystallized pure from toluene; however, **6B** was not obtained free of **6A** or **5**.



6A (*meso*)



6B (*d*,*l*)

Reaction time does not significantly affect the **6A**, **6B**, and **5** product distribution; however, the i-PrNH$_2$:PhPCl$_2$ reactant ratio

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(22) The two independent molecules are in different environments with different intermolecular contacts. For example, O(4) makes relatively short contacts with H(13′) (2.77 Å) and with H(28A) (2.57 Å). No similar contacts are observed for O(4′).

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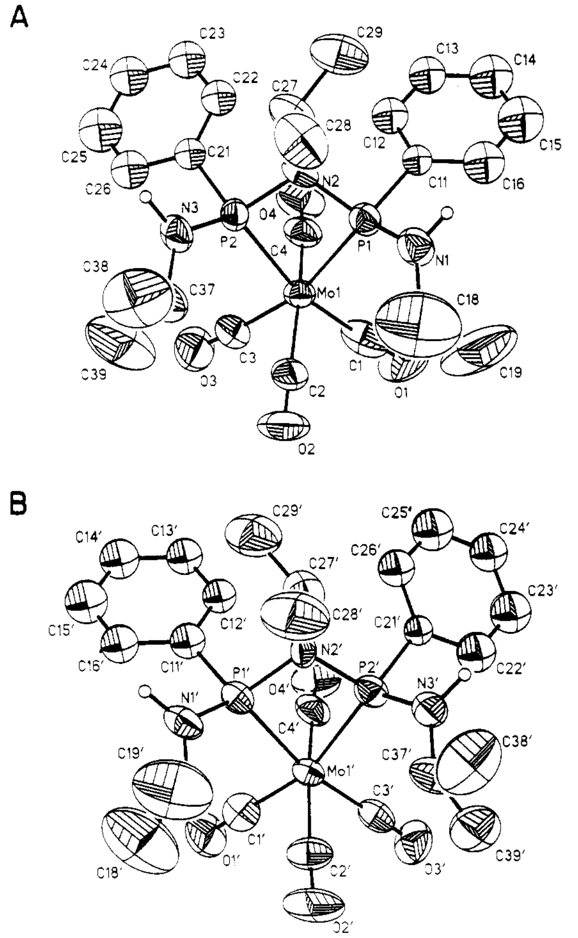

Figure 1. Structure and numbering scheme for *i*-PrN[PhP(*i*-PrNH)]$_2$Mo(CO)$_4$ (**14**): (A) molecule I; (B) molecule II. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms (except on nitrogens) were omitted for clarity.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 $\times$ 10^3) for [PhP(Cl)-*i*-PrNH]$_2$Mo(CO)$_4$ (**15B**)

	x/*a*	*v*/*b*	*z*/*c*	U_{eq}[a]
Mo(1)	−9 (1)	1315 (1)	2242 (1)	41 (1)
P(1)	996 (1)	2824 (1)	3453 (1)	47 (1)
P(2)	−1059 (1)	2937 (1)	1307 (1)	40 (1)
Cl(1)	−913 (1)	3651 (1)	4019 (1)	79 (1)
Cl(2)	821 (1)	4078 (1)	967 (1)	61 (1)
O(1)	1371 (3)	−748 (2)	3430 (2)	95 (1)
O(2)	−3448 (3)	1050 (2)	2896 (2)	101 (1)
O(3)	3392 (2)	1550 (2)	1535 (2)	90 (1)
O(4)	−1240 (3)	−620 (2)	681 (2)	96 (1)
N(1)	2149 (3)	3955 (2)	3217 (1)	56 (1)
N(2)	−2293 (2)	3873 (2)	1709 (1)	50 (1)
C(1)	854 (3)	−1 (2)	2997 (2)	60 (1)
C(2)	−2216 (3)	1152 (2)	2667 (2)	62 (1)
C(3)	2183 (3)	1464 (2)	1789 (2)	55 (1)
C(4)	−790 (3)	78 (2)	1245 (2)	61 (1)
C(11)	2192 (3)	2318 (2)	4444 (2)	51 (1)
C(12)	3797 (3)	2032 (2)	4368 (2)	58 (1)
C(13)	4779 (4)	1539 (2)	5063 (2)	68 (1)
C(14)	4192 (4)	1354 (3)	5822 (2)	79 (1)
C(15)	2631 (5)	1625 (3)	5904 (2)	89 (1)
C(16)	1614 (4)	2114 (3)	5217 (2)	71 (1)
C(17)	2857 (4)	4996 (2)	3820 (2)	62 (1)
C(18)	4676 (4)	5149 (3)	3808 (2)	86 (1)
C(19)	1966 (6)	6121 (3)	3597 (3)	103 (2)
C(21)	−2163 (3)	2509 (2)	211 (1)	45 (1)
C(22)	−3681 (3)	1936 (3)	189 (2)	64 (1)
C(23)	−4559 (4)	1475 (3)	−607 (2)	85 (1)
C(24)	−3908 (5)	1588 (3)	−1373 (2)	89 (1)
C(25)	−2421 (4)	2139 (3)	−1348 (2)	81 (1)
C(26)	−1536 (4)	2607 (2)	−562 (2)	60 (1)
C(27)	−3023 (3)	4932 (2)	1280 (2)	57 (1)
C(28)	−2315 (4)	6101 (3)	1782 (3)	85 (1)
C(29)	−4873 (3)	4835 (3)	1191 (2)	74 (1)

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

and the presence of Et_3N are important. At an *i*-$PrNH_2$:$PhPCl_2$:Et_3N mole ratio of 24:1:15, the **6A**:**6B**:**5** ratio found by ^{31}P NMR spectral integration was 14:1:38. At intermediate reactant ratios, e.g. 2.2:1:2.7, relatively more **6** formed, typically in a ratio of 8:1:6. At lower *i*-$PrNH_2$:$PhPCl_2$ ratios, intermediates containing unreacted P–Cl bonds are also seen in addition to **5** and **6** (see below). In the absence of Et_3N, the **6**:**5** ratio is affected dramatically, although the **6A**:**6B** ratio is not. At a 5:1 *i*-$PrNH_2$:$PhPCl_2$ ratio, **6A**, **6B**, and **5** formed a ratio of 10:1:200. Thus, optimum yields of **6** relative to **5** are attained by using excess Et_3N and with *i*-$PrNH_2$:$PhPCl_2$ ratios of ca. 1.5:1. The highest **6A**:**6B** ratios are attained at the higher amine:$PhPCl_2$ ratio. Under no conditions was **6** formed free of **5**.

The effect of temperature on the **6A**:**6B**:**5** product ratio was examined in reactions carried out at −78, 0, +25, and +110 °C. All reactions were at *i*-$PrNH_2$:$PhPCl_2$:Et_3N ratios of 2.2:1.0:2.2. These yielded **6A**:**6B**:**5** in ratios of 10:1:16 (−78 °C), 8:1:20 (0 °C), 11:1:29 (+25 °C), and 2.3:1:1 (+110 °C), respectively. The **6A**:**6B** ratios do not vary significantly between −78 and +25 °C, but the value at 110 °C is much lower. This is not surprising since at 110 °C, racemization at the phosphorus centers leading to diastereomer equilibration is expected.[9]

Characterization of **5** and **6** as bis(amino)phosphine and bis(phosphino)amine products, respectively, is established by mass, ^1H and ^{31}P NMR spectral data. However, from these data absolute diastereomeric characterization of **6A** and **6B** was not possible. This was achieved by X-ray analysis of the $Mo(CO)_4$ complex of **6A**. Reaction of **6A** with (nor)$Mo(CO)_4$ yields quantitatively the complex *i*-PrN[PhP(*i*-PrNH)]$_2$Mo(CO)$_4$ (**14**). **14**, the exclusive product of the reaction, crystallized from solution to give X-ray quality crystals. These were shown to be characteristic of the bulk sample by repetitive sampling and individual crystal unit cell measurements and by comparing the ^{31}P NMR spectrum of a collection of X-ray quality crystals with the bulk sample spectrum.

The structure of the (**6A**)$Mo(CO)_4$ complex (**14**) is shown in Figure 1. **14** crystallizes as the hemitoluene solvate and with two slightly different molecules of **6A** (I and II) in the unit cell.[22] The complex consists of an *i*-PrN[PhP(*i*-PrNH)]$_2$ moiety cis coordinated to the $Mo(CO)_4$, in a structure in which both Ph groups are on one side and both *i*-PrNH groups are on the opposite side of the Mo–P(1)–P(2)–N(2) ring. The ligand, **6A**, of complex **14** has either *R*,*S* (or *S*,*R*) configurations at phosphorus; hence, it is the *meso* isomer. Complex **14** has approximate C_s point group symmetry; **14-I** and **14-II** differ primarily in the rotation of the *i*-Pr group around the N(2)–C(27) bond. The structural parameters (Table IV) indicate that the structure is similar to those of other known bis(phosphino) molybdenum complexes.[31-33] The mean Mo–P, P–N (terminal) and P–N (P–N–P bridge) distances of 2.498 (5), 1.66 (1), and 1.702 (13) Å are consistent with those in [$(PhNH)_2P]_2NPhMo(CO)_4$.[31] The MoP_2N ring is not planar; the dihedral angle between planes Mo,P(1),P(2) and P(1),N(2),P(2) is 5.8°. The CO groups CO(1), CO(2), and CO(3) are bent back from the bis(phosphine) ligand as expected if there exists substantial intragroup repulsions between CO(1–3) and the two bulky *i*-PrNH groups.

Reaction of *t*-$BuNH_2$ with $PhPCl_2$ and Et_3N was examined under conditions analagous to those that produced **6** from the *i*-$PrNH_2$/$PhPCl_2$ reaction. Reaction occurred stepwise to form compounds that exhibited ^{31}P NMR resonances at δ 155.6, 116.5, and 41.4. By comparison of these resonances to those of other R′P(Cl)NHR[34-37] and $PhP(NHR)_2$ (R, R′ = alkyl and aryl)

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Table IV. Selected Structural Parameters for i-PrN[PhP(i-PrNH)]$_2$Mo(CO)$_4$ (**14**)

	molecule I	molecule II
(a) Bond Distances (Å)		
Mo(1)–P(1)	2.497 (5)	2.503 (5)
Mo(1)–P(2)	2.490 (4)	2.500 (5)
Mo(1)–C(1)	1.973 (21)	1.992 (19)
Mo(1)–C(2)	2.033 (20)	2.027 (19)
Mo(1)–C(3)	1.988 (22)	1.962 (21)
Mo(1)–C(4)	2.009 (22)	2.037 (20)
P(1)–N(1)	1.665 (17)	1.648 (12)
P(1)–N(2)	1.704 (13)	1.715 (12)
P(2)–N(2)	1.700 (13)	1.688 (14)
P(2)–N(3)	1.662 (12)	1.655 (14)
P(1)–C(11)	1.825 (10)	1.792 (12)
P(2)–C(21)	1.819 (12)	1.827 (10)
(b) Bond Angles (deg)		
P(1)–Mo(1)–P(2)	65.1 (2)	65.0 (2)
P(1)–Mo(1)–C(1)	100.4 (6)	98.8 (6)
P(2)–Mo(1)–C(1)	165.2 (6)	162.3 (6)
P(1)–Mo(1)–C(2)	100.8 (6)	98.3 (6)
P(2)–Mo(1)–C(2)	97.8 (5)	99.7 (5)
C(1)–Mo(1)–C(2)	87.2 (8)	89.4 (7)
P(1)–Mo(1)–C(3)	164.0 (6)	165.9 (5)
P(2)–Mo(1)–C(3)	99.3 (6)	100.9 (5)
C(1)–Mo(1)–C(3)	95.0 (9)	95.3 (8)
C(2)–Mo(1)–C(3)	84.2 (8)	83.2 (8)
P(1)–Mo(1)–C(4)	90.8 (6)	93.3 (6)
P(2)–Mo(1)–C(4)	89.8 (6)	88.4 (5)
C(1)–Mo(1)–C(4)	87.8 (8)	85.4 (7)
C(2)–Mo(1)–C(4)	168.1 (8)	167.9 (7)
C(3)–Mo(1)–C(4)	85.5 (8)	86.4 (8)
Mo(1)–P(1)–C(11)	120.7 (4)	118.2 (4)
Mo(1)–P(1)–N(1)	122.6 (5)	124.5 (5)
C(11)–P(1)–N(1)	100.7 (6)	101.4 (7)
Mo(1)–P(1)–N(2)	95.1 (5)	94.8 (5)
C(11)–P(1)–N(2)	104.1 (5)	106.4 (6)
N(1)–P(1)–N(2)	112.6 (7)	110.3 (6)
Mo(1)–P(2)–C(21)	119.8 (4)	118.5 (4)
Mo(1)–P(2)–N(2)	95.4 (4)	95.6 (4)
C(21)–P(2)–N(2)	104.9 (6)	107.6 (6)
Mo(1)–P(2)–N(3)	125.6 (5)	125.4 (5)
C(21)–P(2)–N(3)	98.6 (6)	98.3 (6)
N(2)–P(2)–N(3)	111.1 (6)	110.8 (7)

species,[18,34] and δ 116.5 peak is assigned to the first amination product, PhP(t-BuNH)Cl (**10**).[35] The δ 41.4 resonance is assigned to PhP(t-BuNH)$_2$ (**12**), which was isolated and separately characterized. The δ 155.6 resonance is tentatively assigned to the bis(phosphino)amine t-BuN(PhPCl)$_2$ (**11**), because the chemical shift value is close to that of δ 143.4 reported for MeN(MePCl)$_2$[15] and general bis(phosphino)amines.[15,38] Further reaction produced no evidence for the bis(phosphino)amine analogue of **6**, t-Bu[PhP(t-BuNH)]$_2$. Even after addition of excess t-BuNH$_2$ and Et$_3$N, only **12** and minor amounts of the δ 155.6 compound were seen. It appears likely that reaction to fully aminated bis(phosphino)amine does not occur because of the large steric requirement of the t-Bu groups.

Attempts to obtain bis(phosphino)amines from MeNH$_2$/PhPCl$_2$ and EtNH$_2$/PhPCl$_2$ reactions were unsuccessful. Even in reactions carried out slowly between −78 and +25 °C, complex reaction mixtures formed. The reaction mixtures showed major singlets at δ 67.9 and 64.4, respectively, which by comparison to data for **4** and **5** can be tentatively assigned to PhP(MeNH)$_2$ and PhP(EtNH)$_2$. The minor and ill-defined resonances between δ 78 and 110 could not be interpreted unambiguously, although resonances in this region are generally what would be expected from substituted bis(phosphino)amines **17** (R = Me, Et; R′ = Ph). Attempts to separate and/or characterize these mixtures failed. It seems likely that since the Et and Me groups are smaller than the i-Pr or t-Bu units, reactions of the former are more inclined to go beyond two phosphorus products and form instead higher order condensation products, e.g. rings or extended chains. Although these species are interesting because they might in fact be oligomers and/or polymers of types **1** or **2** sought in P(III) condensation chemistry, we can only speculate about them at this time.

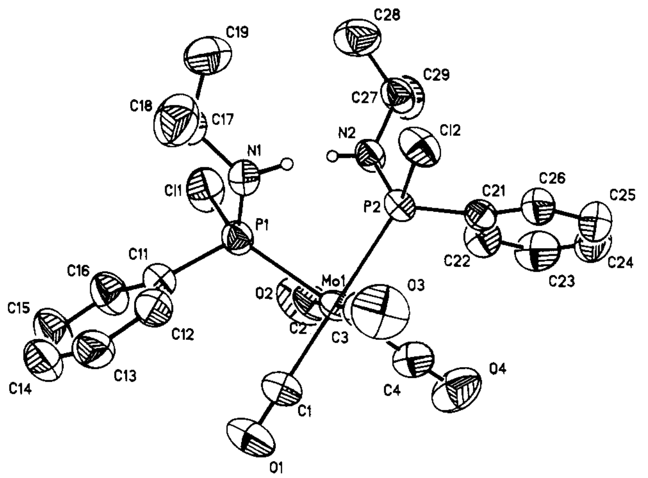

Figure 2. Structure and numbering scheme for [PhP(Cl)-i-PrNH]$_2$Mo(CO)$_4$ (**15B**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms (except on nitrogens) were omitted for clarity.

Aniline (PhNH$_2$) with PhPCl$_2$ (ca. 2:1 mole ratio) in the presence of excess Et$_3$N yields previously reported PhP(PhNH)$_2$ (**4**) and lesser quantities of a product identified as the two diastereomers of the bis(phosphino)amine PhN[PhP(NHPh)]$_2$ (**13A** and **13B**). The **13A** and **13B** mixture exhibited ^{31}P NMR equal-area resonances at δ 62.2 and 61.0, in the region consistent with that expected for a PhP(NHPh)N-type substituted phosphorus center. **13A** was obtained reasonably pure (>90%) and characterized by spectral data. No X-ray quality crystals of either **13A** or **13B** were obtained. Under no conditions did the PhNH$_2$/PhPCl$_2$ reactions show any tendency toward single diastereomer selection. On the basis of correlations of the ^{31}P NMR data with those for **6A** and **6B**, where the *meso* isomer occurs at lower field, we tentatively assign the δ 62.2 and 61.0 ^{31}P NMR resonances to *meso*-**13** (**13A**) and *d,l*-**13** (**13B**), respectively.

Because McFarlane had reported formation of MeN[P(Cl)NMe$_2$]$_2$ as a single unstable diastereomer from reaction of MeN(PCl$_2$)$_2$ with Me$_2$NH,[15] we sought to examine the analogous reactions between PhN(PCl$_2$)$_2$ and Me$_2$NH to see if a more stable product, because of the possible stabilizing influence of the Ph group, could be obtained. However, the reaction was not clean, and a resonance clearly attributable to PhN[P(Cl)NMe$_2$]$_2$ was not present. With Me$_2$NH in the presence of Et$_3$N, mixtures yielding major ^{31}P NMR spectral resonance at δ 199.6, 164.9, and 155.4 due to (PhNPCl)$_2$,[10c,34] Me$_2$NPCl$_2$,[10d] and unreacted PhN(PCl$_2$)$_2$,[10c] respectively, formed. The diazadiphosphetidine (PhNPCl)$_2$ likely formed by base-promoted elimination of HCl from acyclic chloroaminophosphine intermediates and is not unexpected. The remaining minor equal-area coupled doublets at δ 152.2 and 133.7 (J = 70 Hz) could not be assigned.

Reactions of i-PrNH$_2$ with PhPCl$_2$, at low reactant ratios (i-PrNH$_2$ < PhPCl$_2$), provided insight into the series of reactions by which *meso*-**6** and *d,l*-**6** form. At a 1:1:1 i-PrNH$_2$:PhPCl$_2$:Et$_3$N ratio, the reaction yields a mixture that exhibits ^{31}P{^{1}H} NMR spectral singlet resonances at δ 128, 126, 124, 121.1, 68, and 65 in addition to a resonance for unreacted PhPCl$_2$. At the lower reactant ratios, only the δ 121.1 resonance and a resonance for unreacted PhPCl$_2$ are evident. Because the δ 121.1 peak forms early in the reaction and is in the region expected for an aminochlorophenylphosphine, it is assigned to PhP(i-PrNH)Cl (**7**).

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Table V. Selected Structural Parameters for $[PhP(Cl)\text{-}i\text{-}PrNH]_2Mo(CO)_4$ (**15B**)

(a) Bond Lengths (Å)

Mo(1)–P(1)	2.459 (1)	Mo(1)–P(2)	2.463 (1)
Mo(1)–C(1)	1.999 (3)	Mo(1)–C(2)	2.035 (3)
Mo(1)–C(3)	2.043 (3)	Mo(1)–C(4)	2.013 (3)
P(1)–Cl(1)	2.122 (1)	P(1)–N(1)	1.639 (2)
P(1)–C(11)	1.817 (2)	P(2)–Cl(2)	2.117 (1)
P(2)–N(2)	1.637 (2)	P(2)–C(21)	1.825 (2)
O(1)–C(1)	1.145 (3)	O(2)–C(2)	1.131 (4)
O(3)–C(3)	1.130 (3)	O(4)–C(4)	1.139 (3)

(b) Bond Angles (deg)

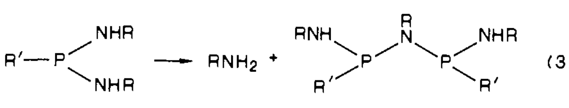
P(1)–Mo(1)–P(2)	90.5 (1)	P(1)–Mo(1)–C(1)	89.6 (1)
P(2)–Mo(1)–C(1)	179.7 (1)	P(1)–Mo(1)–C(2)	91.3 (1)
P(2)–Mo(1)–C(2)	89.7 (1)	C(1)–Mo(1)–C(2)	90.7 (1)
P(1)–Mo(1)–C(3)	89.9 (1)	P(2)–Mo(1)–C(3)	89.9 (1)
C(1)–Mo(1)–C(3)	89.8 (1)	C(2)–Mo(1)–C(3)	178.8 (1)
P(1)–Mo(1)–C(4)	178.9 (1)	P(2)–Mo(1)–C(4)	89.7 (1)
C(1)–Mo(1)–C(4)	90.2 (1)	C(2)–Mo(1)–C(4)	89.7 (1)
C(3)–Mo(1)–C(4)	89.1 (1)	Mo(1)–P(1)–Cl(1)	113.1 (1)
Mo(1)–P(1)–N(1)	116.5 (1)	Cl(1)–P(1)–N(1)	104.9 (1)
Mo(1)–P(1)–C(11)	118.7 (1)	Cl(1)–P(1)–C(11)	99.3 (1)
N(1)–P(1)–C(11)	102.0 (1)	Mo(1)–P(2)–Cl(2)	113.0 (1)
Mo(1)–P(2)–N(2)	116.9 (1)	Cl(2)–P(2)–N(2)	104.2 (1)
Mo(1)–P(2)–C(21)	118.3 (1)	Cl(2)–P(2)–C(21)	99.6 (1)
N(2)–P(2)–C(21)	102.5 (1)	P(1)–N(1)–C(17)	126.9 (2)
P(2)–N(2)–C(27)	126.3 (2)	Mo(1)–C(2)–O(2)	179.2 (2)
Mo(1)–C(1)–O(1)	179.0 (2)	Mo(1)–C(4)–O(4)	179.7 (4)
Mo(1)–C(3)–O(3)	179.7 (2)		

Although we were not successful in isolating pure **7**, it was possible to characterize it indirectly as the $Mo(CO)_4$ complex. Reaction of **7** with $(nor)Mo(CO)_4$ in toluene at 25 °C yields $[PhP(Cl)NH\text{-}i\text{-}Pr]_2Mo(CO)_4$ (**15**) as two diastereomers, **15A** and **15B**, in an equimolar ratio. Crystallization from toluene yielded pure **15B**.

X-ray analysis of **15B** shows it to be the *d,l* diastereomer of a complex that contains two PhP(Cl)NH-*i*-Pr molecules cis-bonded to the $Mo(CO)_4$ unit (Figure 2). Selected structural parameters are listed in Table V. The structural features are generally typical for a molybdenum(0)-coordinated aminophosphine. The mean Mo–P distance of 2.46 Å is close to that seen in molybdenum complexes such as $(CO)_3Mo(PCl_3)_3$,[39] $[(PhNH)_2P]_2NPhMo(CO)_4$,[31] and $i\text{-}PrN[PhP(i\text{-}PrNH)]_2Mo(CO)_4$, above. The ligand distribution around Mo is close to perfectly octahedral. No significant distortion as a result of intragroup repulsions, as was the case with *meso*-**6**, are seen. The P–Mo–P angle is 90.5° and all cis C–Mo–C angles are within 1° of 90°.

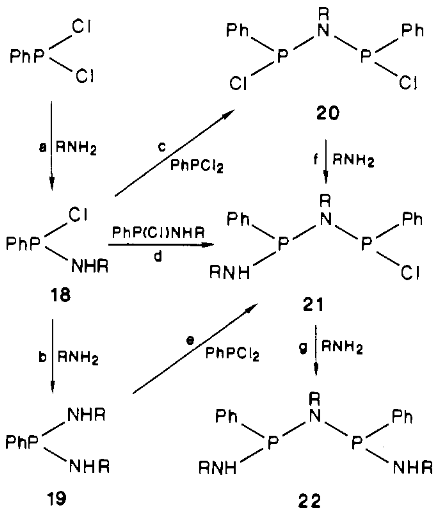
With complete characterization of **7**, **5**, and **6**, it becomes possibly to tentatively characterize other intermediates in the overall reaction. The δ 128, 126, and 124 resonances are all in the aminochlorophenylphosphine [()NP(Ph)Cl] chemical shift region.[34-37] One of these, the sharp singlet at δ 124, likely arises from the symmetrical $i\text{-}PrN(PhPCl)_2$ (**8**). The resonances at δ 68 and 65 are in the bis(amino)phenylphosphine $[()N)_2PPh]$ region. Thus these, along with equal-area peaks at δ 128 and 126, could be the expected pairs of resonances for diastereomers of the unsymmetrical $i\text{-}PrN[PhP(i\text{-}PrNH)](PhPCl)$ (**9**). At low ratios of $i\text{-}PrNH_2{:}PhPCl_2$, very little **6** and **5** are seen; however, upon addition of $i\text{-}PrNH_2/Et_3N$ to these mixtures, resonances due to these final products appear and the peaks due to intermediates disappear.

Thermolysis of **4** and **5** in separate experiments was studied in order to determine if condensation with elimimation of RNH_2 could occur (eq 3) and be a possible route by which condensation to P–N–P-unit-containing molecules occurs. **5** was heated at 130 °C for 4 days, during which time slow conversion to **6A** and **6B** occurred. Similarly, **4** when heated at 130–140 °C for 4.5 days, underwent partial conversion to **13A** and **13B**. Both **6** and **13** were obtained cleanly and in the near absence of other products; however, in neither case was the bis(phosphino)amine formed with diastereomeric selectivity. Since these reactions are not diastereomerically selective, they likely are not reaction types by which *meso*-**6** (**6A**) is formed preferentially in the $i\text{-}PrNH_2\text{–}PhPCl_2$ reactions.



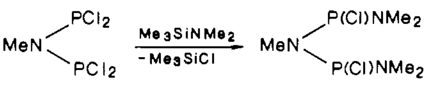
(3)

Scheme I



Although isolation and unambiguous characterization of intermediates in the $RNH_2\text{–}PhPCl_2$ reactions is so far limited to $PhP(Cl)NH\text{-}i\text{-}Pr$ (**7**), $PhP(NH\text{-}i\text{-}Pr)_2$ (**5**), and $i\text{-}PrN[PhP(i\text{-}PrNH)]_2$ (**6**) from the $i\text{-}PrNH_2/PhPCl_2$ reaction and $PhP(t\text{-}BuNH)_2$ (**12**) from the $t\text{-}BuNH_2\text{–}PhPCl_2$ reaction, these data along with other solution spectral data allow us to suggest a general scheme for the $RNH_2\text{–}PhPCl_2$ reactions. Since direct elimination of RNH_2 between aminophosphines (eq 3) occurs only with difficulty, it appears that P–N bond formation occurs through P–Cl + N–H type condensation processes. A reasonable sequence is shown in Scheme I. $PhPCl_2$, in stepwise aminations, yields the mono and bis(amino) species **18** and **19** in steps a and b. Subsequently, the $PhP(Cl)NHR\text{–}PhPCl_2$ reaction (c) could yield symmetrical $RN(PhPCl)_2$ (**20**), and the PhP(Cl)NHR–PhP(Cl)NHR reaction (d) and/or the $PhP(NHR)_2\text{–}PhPCl_2$ reaction (e) could produce unsymmetrical RN(PhPCl)[PhPNHR] (**21**). Finally, amination of terminal P–Cl bonds of the bis(phosphino) products (reactions f and g) would yield product **22**. At this stage of our understanding, participation of all species and routes must be considered.

It is especially interesting to consider at what point in the formation of **6** that diastereomer selection of **6A** occurs and why similar selection in the formation of $PhN[PhP(NHPh)]_2$ (**13**) does not occur. Diastereomer selection might occur because of conformation selection (excess population of one rotamer) in either intermediate or transition-state P–Cl-bond-containing species. Diastereomer selection could occur in P–N bond formation reactions involving either or both terminal P–N bonds (e.g. steps f and g) or P–N–P bonds (e.g. steps c, d, or e). Clearly, the fact that McFarlane obtains one diastereomer, $MeN[P(Cl)NMe_2]_2$, from the $MeN(PCl_2)_2/Me_3SiNMe_2$ reaction[15] suggests that terminal bond formation in that reaction can be involved (eq 4).



(4)

However, until intermediate reaction species can be fully isolated and characterized and the exact order of their involvement in the reaction established, the diastereoselective route to **6A** cannot be detailed. It is possible that, through variations in substitution and/or through use of other bis(phosphino) formation reactions, ways will be found to control diastereomer formation so that either

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meso or *d,l* isomers can be selectively formed. Further studies are in progress and will be reported later.

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Supplementary Material Available: Listings of crystal structure data and details of the determination, positional parameters, anisotropic thermal parameters, hydrogen atom parameters, bond distances, bond angles, and least-squares equations and planes (20 pages); listings of calculated and observed structure factors (49 pages). Ordering information is given on any current masthead page.

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Crystal Structures of $XeF_5^+MF_4^-$ (M = Ag, Au) and Their Relevance to the Basicity and Oxidizability of MF_4^-

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$XeF_5^+AuF_4^-$ has been prepared from $BrF_3{\cdot}AuF_3$ by displacement of BrF_3 with XeF_6. The salt interacts quantitatively with KrF_2 in anhydrous HF, below 0 °C, to yield $XeF_5^+AuF_6^-$. XeF_5AuF_4 (I) is isostructural with XeF_5AgF_4 (II), and these compounds crystallize in space group $I4/m$ with the following unit cell dimensions: I, $a_0 = 5.735$ (5) Å, $c_0 = 20.007$ (17) Å, $V = 658$ (2) Å^3, $Z = 4$; II, $a_0 = 5.593$ (2) Å, $c_0 = 20.379$ (5) Å, $V = 637.5$ (8) Å^3, $Z = 4$. The structure of II was solved by the Patterson method and refined to conventional R and R_w values of 0.077 and 0.090, respectively. The structure contains double layers of XeF_5^+ and layers of AgF_4^- ions, all layers being parallel to the *ab* plane. The XeF_5^+ ion had C_{4v} symmetry with Xe–F(axial) = 1.853 (19) Å, Xe–F(equatorial) = 1.826 (9) Å, and F(axial)–Xe–F(equatorial) = 77.7 (3)°. The anion (site symmetry D_{2h}), which is not significantly different from D_{4h} symmetry, has Ag–F = 1.902 (11) Å. Differences between the XeF_5AgF_4 and XeF_5AuF_4 structures are attributed to lower ligand charges in the anion of the former, relative to those in the latter, and these in turn are related to observed differences in the basicity and oxidizability of the anions.

Introduction

Krypton difluoride has the lowest mean thermochemical bond energy[1] of any known fluoride and is an oxidizer of extraordinary power.[2] The demonstration by Bougon and his co-workers[3] of the effectiveness of KrF_2 as an oxidative fluorinator in the production of a binary fluoride of silver, of composition close to that of AgF_3, suggested that it might also be valuable in the generation of even higher oxidation states of silver in anionic species.

Since Ag(V) had been claimed by Hagenmuller and his co-workers,[4] in the diamagnetic antifluorite-structure materials Cs_2AgF_6 and $Cs_2Ga_{0.5}Ag_{0.5}F_6$, it was anticipated that KrF_2 would be capable of generating AgF_6^- under suitably basic conditions. In an attempt to produce the silver relative of the first Au(V) salt,[5] $Xe_2F_{11}^+AuF_6^-$, AgF_2 was treated with KrF_2 in anhydrous HF (AHF) in the presence of the fluoro base XeF_6. The product was[6] $XeF_5^+AgF_4^-$.

Although many AuF_4^- salts are known,[7-9] the gold relative of $XeF_5^+AgF_4^-$ was not. On the other hand, the Au(V) salt $XeF_5^+AuF_6^-$ was known.[10]

It appeared that if $XeF_5^+AuF_4^-$ could be prepared, it would be a structural relative of $XeF_5^+AgF_4^-$. The high thermal stability[10] of $XeF_5^+AuF_6^-$ also suggested that its preparation from $XeF_5^+AuF_4^-$ would be readily achieved by using KrF_2. These expectations have been realized. In addition the structural relationship of $XeF_5^+AgF_4^-$ to $XeF_5^+AuF_4^-$ has shed light on the factors that cause AgF_4^- both to be a poor base and to be difficult to oxidize.

Experimental Section

1. Apparatus and Reagents. A nickel vacuum line was used. It had a mercury diffusion pump, a mechanical pump, and soda–lime scrubbers (for removal of fluorine, HF, and oxidizing fluorides) and was equipped with a Monel Acco Helicoid pressure gauge (0–1400 Torr, ±0.3%) and nickel valves with Teflon packing. Teflon FEP reaction vessels (18 mm o.d.) equipped with Teflon valves were used for all preparations. AgF_2 (99.5% purity; Fluka, Buchs, Switzerland) was used as supplied. KrF_2 was prepared[11] by irradiation of a liquefied mixture of fluorine and krypton with near-UV light at −196 °C. XeF_6 was prepared by the interaction of xenon with fluorine, in the presence of NiF_2 as a catalyst,[12] at 120 °C. F_2 was prepared and purified as described elsewhere.[13] Additional purification was performed by photolysis (to make O_2F_2 from O_2 impurity).[14] Xenon and krypton (each 99.99%) were used as supplied (Messer Griesheim, Linz, Austria). Anhydrous hydrogen fluoride (Kalie Chemie, Hannover, Germany) was purified as described previously[15] and then treated with KrF_2. Bromine trifluoride was prepared by the fluorination of bromine at ambient temperatures in a nickel vessel.

2. Instrumentation. Raman spectra were obtained with use of a Spex 1401 double monochromator, and a detection system that utilized photon-counting techniques was used in conjunction with a variety of laser lines (Coherent Radiation; principally 488.0, 514.5, and 647.1 nm). Powdered samples were loaded into 1 mm i.d. quartz capillaries in the drybox, and the capillaries were sealed temporarily with a plug of Kel-F grease and then drawn and sealed in a small flame outside the drybox.

X-ray Powder Photography. X-ray powder diffraction patterns of solid samples were obtained with an Enraf apparatus (Delft, Holland), using graphite-monochromatized Cu Kα radiation. A finely powdered sample was sealed into 0.5-mm quartz capillaries as described for Raman spectroscopy.

3. Preparation of $XeF_5^+AgF_4^-$ Single Crystals. The compound $XeF_5^+AgF_4^-$, as previously described,[6] was weighed into a FEP apparatus,

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