Diastereoselectivity in the Formation of Skeletally Stabilized Phosphazanes

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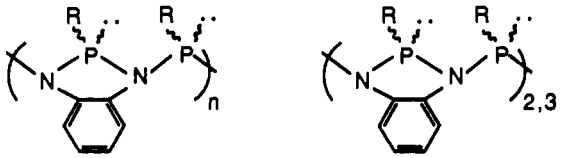
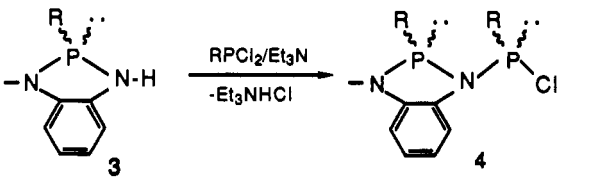
Skeletally stabilized di- and triphosphazane formation and stereoselection from reactions of phosphadiazoles $C_6H_4(NH)_2PPh$ (**7**), $C_6H_4(NH)_2P(S)Ph$ (**8**), $C_6H_4(NH)(MeN)PPh$ (**9**), and $C_6H_4(NH)(MeN)P(S)Ph$ (**10**) with $PhPCl_2$, Ph_2PCl, and $PhP(Et_2N)Cl$ have been examined. Reaction of **9** with $PhPCl_2/Et_3N$ yields 1:1 *threo*- (**14a**) and *erythro*-chlorodiphosphazane (**14b**) $C_6H_4(MeN)[NP(Cl)Ph]PPh$, and 5:1 *threo,threo-meso* (**15a**) and *d,l* (**15b**) isomers of triphosphosphazane $[C_6H_4(N)(MeN)PPh]_2PPh$. Reactions of **7**/$PhPCl_2/Et_3N$ or **7**/$PhP(Et_2N)Cl$ yield 1:1 mixtures of the highly reactive chlorodiphosphazanes *threo*- (**13a**) and *erythro*- $C_6H_4(NH)[NP(Cl)Ph]PPh$ (**13b**); **7** with Ph_2PCl/Et_3N forms $C_6H_4(NH)(NPPh_2)PPh$ (**11**) and $C_6H_4(NPPh_2)_2PPh$ (**12**). Phosph(V)adiazole **8** with $PhPCl_2/Et_3N$ yields one isomer of $C_6H_4(NH)[NP(Cl)Ph]P(S)Ph$ (**17**) and a 2:1 mixture of one *meso* (**18a**) and the *d,l* (**18b**) isomer of triphosphazane $C_6H_4[NP(Cl)Ph]_2P(S)Ph$; the **8**/Ph_2PCl reaction forms $C_6H_4(NPPh_2)_2P(S)Ph$ (**16**). The **10**/$PhPCl_2/Et_3N$ reaction produces 5:1 *threo*- (**19a**) and *erythro*- $C_6H_4(MeN)[NP(Cl)Ph]P(S)Ph$ (**19b**). Compounds **11**–**19** were characterized by spectral data; absolute stereochemistry of **15a** was determined by X-ray analysis: triclinic, $P\bar{1}$, $a = 10.369(2)$ Å, $b = 12.326(3)$ Å, $c = 12.682(6)$ Å, $\alpha = 76.58(3)°$, $\beta = 70.52(3)°$, $\gamma = 81.11(2)°$, $V = 1481.1(8)$ Å^3, $Z = 2$, $R = 0.0526$, $R_w = 0.0648$. The stereochemistry of **19a** was established from X-ray analysis of its molybdenum complex $C_6H_4(MeN)[NP(Cl)Ph]P(S)PhMo(CO)_4$ (**20a**): monclinic, $P2_1/c$, $a = 11.056(2)$ Å, $b = 11.991(3)$ Å, $c = 19.583(3)$ Å, $\beta = 100.310(10)°$, $V = 2554.2(7)$ Å^3, $Z = 4$, $R = 0.0413$, $R_w = 0.0493$. Although chlorodiphosphazane formation from phosph(III)adiazole chlorophosphination is nonselective, the analogous reaction involving phosph(V)diazoles is selective, favoring *threo* isomer formation. Comparison of skeletally stabilized phosphazane formation is made to that of previously reported acyclic analogs. Implications of the observed stereoselectivity for higher skeletally stabilized phosphazane formation are discussed.

Introduction

Skeletally stabilized acyclic oligomeric/polymeric (**1**)[1-3] and cyclic (**2**)[4-8] phosph(III)azanes are produced in reactions of 1,2-$(NH_2)_2C_6H_4$ with alkylphosphorus dichlorides ($RPCl_2$), in a

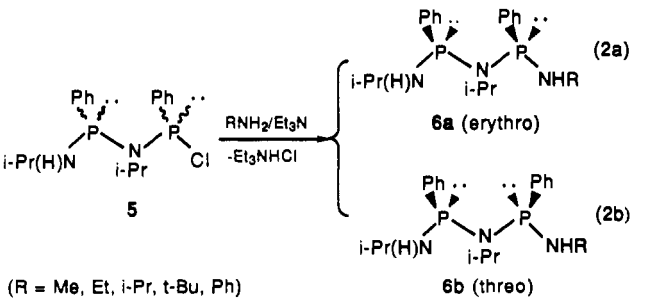


process where phosphorus–nitrogen bonds form by chlorophosphine–amine condensations. The reactions apparently proceed via rapid initial formation of phosphadiazoles (**3**)[5a,6] followed by phosphorus–nitrogen chain extension in slower phosphadiazole–chlorophosphine reactions, e.g. eq 1. Since it was demonstrated



(1)

recently that *erythro* (*meso*) diphosphazanes **6a** are formed preferentially in reactions of primary amines (RNH_2) with the chlorodiphosphazane **5** (eq 2),[9-11] it is of interest to determine if



(2a)

(2b)

(R = Me, Et, i-Pr, t-Bu, Ph)

analogous stereoselectivity might be expressed in the condensation processes that produce skeletally stabilized phosphazanes. In the latter reactions, chlorodiphosphazanes or chlorodiphosphazane units (e.g. **4**) might form; subsequently during amination by phosphadiazoles, stereocontrol might be exerted over the phosphorus R-group orientations along the phosphazane chain.

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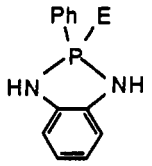
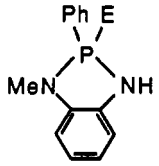
In order to determine (i) the extent to which stereoselection occurs in the formation of skeletally stabilized di- and triphosphazanes, (ii) whether stereoselection occurs only in P–Cl bond aminations or also in transaminative processes, and (iii) the stage in the condensation process(es) where selection occurs, we undertook studies of diphosphazanes and triphosphazanes formed from reactions between phosph(III)adiazoles (**7**, **9**) and phosph(V)adiazoles (**8**, **10**) and $PhPCl_2$, $PhP(NEt_2)Cl$, and Ph_2PCl. The results of these studies are reported below.



7, E = LP
8, E = S



9, E = LP
10, E = S

Experimental Section

Apparatus and Materials. Phosphorus-31 and ^1H NMR spectra were recorded with a Varian VXR300 spectrometer operating at 121.2 and 300 MHz, respectively. ^{31}P and ^1H chemical shifts downfield from 85% H_3PO_4 (external) and Me_4Si (internal) are reported as positive (+δ). IR spectra (4000–400 cm^{-1}) were obtained using a Beckman 4250 or an IBM IR/32 Type 9132 spectrometer. Mass spectra were obtained at 70 eV with a Varian MAT-CH5 or a VG Analytical 7070 EQ-HF spectrometer. Mass spectal data refer to the major peak of the respective envelope. Exact mass analyses were referenced to perfluorokerosene. X-ray diffraction data were collected on a Nicolet (Siemens) P3/F automated diffractometer equipped with a graphite monochrometer. All manipulations were carried out using glovebag or Schlenk techniques under dry N_2.[12]

Flash chromatography was carried out according to the method of Still et al.[13] A 650- or 450-mL column was packed with 15 cm of silica gel 60 (230–400 mesh). Compounds were eluted with the necessary solvent mixture under N_2 pressure at 2.0 ± 0.1 in./min. Fractions (25 mL) were collected, analyzed by TLC, and combined according to their R_f values.

$1,2\text{-}(NH_2)_2C_6H_4$ (Aldrich) was recrystallized from toluene and sublimed before use. Toluene (over Na/benzophenone), tetrahydrofuran (over Na/benzophenone, Mallinckrodt), $PhPCl_2$ (Aldrich), Ph_2PCl (Aldrich), and CH_2Cl_2 (P_4O_{10}) were distilled before use. Silica gel (EM Science), $o\text{-}C_6H_4(NH_2)(MeNH)\cdot 2HCl$, *n*-BuLi (1.6 M in hexane), hexanes, and deuterated solvents were used as received. $C_6H_4(NH)_2PPh$ (**7**),[1c] $o\text{-}C_6H_4(NH_2)(MeNH)$,[14] $C_6H_4(NH)_2P(S)Ph$ (**8**),[1c,15] $C_6H_4(NH)(MeN)PPh$ (**9**),[16] and $C_6H_4(NH)(MeN)P(S)Ph$ (**10**) were prepared by new methods or modifications of reported procedures (see below). $PhP(NMe_2)_2$,[17] $PhP(NEt_2)_2$,[17] and (norbornadiene)$Mo(CO)_4$[18] were prepared as described previously.

Preparation of $C_6H_4(NH)_2PPh$ (7). $PhP(NMe_2)_2$ (0.286 g, 1.5 mmol) and 1,2-diaminobenzene (0.185 g, 1.7 mmol) were heated in toluene (30 mL) for 3 days at 95 °C with occasional venting. Since isolated **7** decomposed rapidly, it was used directly in solution in subsequent reactions; prior to use, Me_2NH that formed during reaction was removed in vacuo and reaction byproduct solids were removed by filtration.

Preparation of $o\text{-}C_6H_4(NH_2)(MeNH)$. Butyllithium (18.2 mL, 29.2 mmol) was added dropwise at 0 °C to a stirred THF solution (100 mL) of $o\text{-}C_6H_4(NH_2)(MeNH)\cdot 2HCl$ (2.8355 g, 14.6 mmol). After 1 h, the THF was removed in vacuo and $o\text{-}C_6H_4(NH_2)(MeNH)$ was extracted into toluene. After removal of toluene, the orange liquid $o\text{-}C_6H_4(NH_2)(MeNH)$ was vacuum-distilled at 68 °C (0.1 mmHg). ^1H NMR (toluene-d_8): δ 2.2 (d, 3H; CH_3), 2.7 (broad s, 2H; NH_2), 2.9 (broad s, 1H; CH_3NH), 6.2–6.7 (m, 4H; aryl).

Preparation of $PhP(NEt_2)Cl$. $PhPCl_2$ (0.14 mL, 1.04 mmol) and $PhP(NEt_2)_2$ (0.27 mL, 1.04 mmol) were allowed to react in toluene (10 mL) for 5 min. $PhP(NEt_2)Cl$ formed quantitatively. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 140 (s). ^1H NMR (toluene-d_8): δ 0.80 (t, 6H, $^3J_{HH}$ = 7.1 Hz), 2.85 (d of q, 4H, $^3J_{PH}$ = 14.2), 7.0–7.2 (m, 3H), 7.6–7.7 (m, 2H). MS (EI$^+$): M^+ *m/e* 215.

Preparation of $C_6H_4(NH)(MeN)PPh$ (9). $o\text{-}C_6H_4(NH_2)(MeNH)$ (0.25 mL, 2.1 mmol) and $PhP(NEt_2)_2$ (0.55 mL, 2.1 mmol) were heated in toluene (50 mL) at 95 °C for 20 h, after which Et_2NH was removed in vacuo. The $^{31}P\{^1H\}$ NMR spectrum exhibited a major resonance at δ 91.6 (>70% area, **9**) and other resonances at δ 10–20 attributable to oxidized phosphorus products. Attempts to isolate **9** by fractional crystallization and silica-gel flash chromatography failed. Yields of **9** were estimated by $^{31}P\{^1H\}$ NMR spectral integrals.

Reactions of 7. (A) With Ph_2PCl To Form $C_6H_4(NH)(NPPh_2)PPh$ (11) and $C_6H_4(NPPh_2)_2PPh$ (12). A toluene solution (10 mL) of **7** (2.1 mmol) was added dropwise to a toluene solution (100 mL) of Ph_2PCl (0.75 mL, 4.2 mmol) and Et_3N (0.63 mL, 4.5 mmol). The mixture was stirred for 5 min at 25 °C. Et_3NHCl was removed by filtration, and the solution was concentrated in vacuo. The $^{31}P\{^1H\}$ NMR spectrum showed equal-area resonances at δ 88.5 (d, $^2J_{PP}$ = 87 Hz, 1P) and 43.3 (d, 1P) attributable to **11** (69% spectral area), δ 96.5 (t, $^2J_{PP}$ = 50 Hz, 1P) and 41.8 (d, 2P) attributable to **12** (23% spectral area), and unassignable resonances between δ 10 and δ 20.

(B) With $PhP(NEt_2)Cl$ To Form $C_6H_4(NH)[NP(Cl)Ph]PPh$ (13). **7** (1.04 mmol) in toluene (10 mL) was added dropwise at 25 °C to $PhP(NEt_2)Cl$ (2.08 mmol) in toluene (10 mL) in a reactor open to a Schlenk line vacuum. The $^{31}P\{^1H\}$ NMR spectrum exhibited resonances from two diastereomers of **13**: **13a**, δ 114.3 (d, $^2J_{PP}$ = 170.0 Hz, 1P), 90.6 (d, 1P); **13b**, δ 117.3 (d, $^2J_{PP}$ = 80.0 Hz, 1P), 89.0 (d, 1P); ratio **13a:13b** = 1:1; total spectral area ~35%; other broad, unassigned resonances. **13a/b** could not be isolated; upon standing it slowly converted to **2**.[5]

In the presence of Et_3N, **7** (1.5 mmol) and $PhP(NEt_2)Cl$ (3.0 mmol) react during 12 h at 25 °C to form a mixture of uncharacterized phosphazane products; ^{31}P NMR spectral resonances occur between δ 78 and δ 93.

(C) With $PhP(NEt_2)_2$. Thermolysis of **7** and $PhP(NEt_2)_2$ in toluene at 90 °C for 150 h yields an uncharacterizable reaction mixture.

(D) With $PhP(S)Cl_2$. **7** (1.04 mmol) with $PhP(S)Cl_2$ (0.32 mL, 2.08 mmol) and Et_3N (0.29 mL, 2.1 mmol) in toluene underwent no reaction during 150 h at 70 °C, as determined by ^{31}P NMR analysis.

Reaction of 9 with $PhPCl_2$ To Form $C_6H_4(MeN)[NP(Cl)Ph]PPh$ (14) and $[C_6H_4(N)(MeN)PPh]_2PPh$ (15). **9** (1.4 mmol) in toluene (10 mL) was added to a toluene solution (50 mL) of $PhPCl_2$ (0.095 mL, 0.7 mmol) and Et_3N (0.21 mL, 1.5 mmol) at 0 °C. After 5 min, the $^{31}P\{^1H\}$ NMR spectrum showed resonances from the two diastereomers of **14**: **14a**, δ 115.0 (d, $^2J_{PP}$ = 80 Hz, 1P), 101.0 (d, 1P); **14b**, δ 113.0 (d, $^2J_{PP}$ = 126 Hz, 1P), 101.5 (d, 1P); ratio **14a:14b** = 1:1; total spectral area ~50%. Resonances were also present from **15** (spectral area 20%) and unreacted **9**. After 30 min, the reaction mixture contained only diastereomers **15a** and **15b** (**15a:15b** = 5:1). The solution was filtered through silica gel; X-ray quality crystals of **15a** were obtained from toluene. **15a**: $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 80.0 (t, $^2J_{PP}$ = 26 Hz, 1P), 98.5 (d, 2P); ^1H NMR (toluene-d_8) δ 2.55 (t, $^3J_{HP}$ = 6.0 Hz, 6H), 6.1–7.4 (m, 23H); MS (EI$^+$): M^+ *m/e* 562. Anal. Calcd for $C_{32}H_{29}P_3N_4$: mol wt 562.1605. Found: mol wt (exact mass MS) 562.1601. Mp = 156 °C. Since **15b** was not obtained free of **15a**, it was characterized only by NMR spectral data. **15b**: $^{31}P\{^1H\}$ NMR (toluene-d_8) AMX[19] pattern; δ 97.9 (d, 1P, $^2J_{AM}$ = 72.0 Hz; P_A), 92.7 (d of d, 1P; P_M), 74.7 (d, 1P, $^2J_{MX}$ = 19.0 Hz; P_X).

Synthesis of 14a/14b. Addition of $o\text{-}C_6H_4(NH_2)(MeNH)$ (0.22 mL, 1.85 mmol) to $PhPCl_2$ (0.50 mL, 3.7 mmol) and Et_3N (0.77 mL, 5.5 mmol) in toluene (30 mL) at 0 °C yields **14a/14b** (>90% spectral area) in a 1:1 ratio. $^{31}P\{^1H\}$ NMR (toluene-d_8): **14a**, δ 115.0 (d, $^2J_{PP}$ = 80 Hz, 1P), 101.0 (d, 1P); **14b**, δ 113.0 (d, $^2J_{PP}$ = 126 Hz, 1P), 101.5 (d, 1P). MS (EI$^+$): M^+ *m/e* 370.

Reactions of 8. (A) With Ph_2PCl To Form $C_6H_4(NPPh_2)_2P(S)Ph$ (16). A toluene solution (10 mL) of **8** (0.5166 g, 2.1 mmol) was added to Ph_2PCl (0.75 g, 4.2 mmol) and Et_3N (0.63 mL, 4.5 mmol) in toluene (30 mL), and the mixture was heated at 70 °C. After 1 h, the $^{31}P\{^1H\}$

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Table 1. Crystal Data and Details of Structure Determinations for $[C_6H_4(N)(MeN)PPh]_2PPh$ (**15a**) and $C_6H_4(MeN)[NP(Cl)Ph]P(S)PhMo(CO)_4$ (**20a**)

	15a	**20a**
formula	$C_{32}H_{29}N_4P_3$	$MoC_{23}H_{17}N_2O_4P_2SCl$
fw	562.5	610.8
space group	$P\bar{1}$	$P2_1/c$
crystal system	triclinic	monoclinic
a, Å	10.369(2)	11.056(2)
b, Å	12.326(3)	11.991(3)
c, Å	12.682(6)	19.583(3)
α, deg	76.58(3)	90.0
β, deg	70.52(3)	100.310(10)
γ, deg	81.11(2)	90.0
V, Å^3	1481.1(8)	2554.2(7)
Z	2	4
d_{calc}, g/cm^3	1.261	1.588
μ, cm^{-1}	2.22	8.39
λ(Mo Kα), Å	0.710 73	0.710 73
temp, °C	24–26	22–24
R, R_w[a]	0.0526, 0.0648	0.0413, 0.0493

[a] R and R_w are for observed data.

NMR spectrum showed resonances attributed to **16** (80% spectral area) at δ 94 (t, $^2J_{PP}$ = 91, 1P) and 36 (d, 2P) and $Ph_2PP(O)Ph_2$ (20% spectral area) at δ 36.0 ($^1J_{PP}$ = 218 Hz, 1P) and −20 (d, 1P). No attempt was made to isolate **16**.

(B) With $PhPCl_2$ To Form $C_6H_4(NH)[NP(Cl)Ph]P(S)Ph$ (17) and $C_6H_4[NP(Cl)Ph]_2P(S)Ph$ (18). A toluene solution (10 mL) of **8** (0.108 g, 0.44 mmol) was added dropwise to $PhPCl_2$ (0.12 mL, 0.88 mmol) and Et_3N (0.12 mL, 0.90 mmol) in toluene (30 mL) at 0 °C. After the mixture was warmed to 25 °C, the Et_3NHCl was removed by filtration. The $^{31}P\{^1H\}$ NMR spectrum exhibited resonances attributable to two diastereomers of **18**: **18a**, δ 88.0 (t, $^2J_{PP}$ = 112 Hz, 1P), 102.5 (d, 2P); **18b**, δ 86.6 (d of d, $^2J_{PP}$ = 116.5 Hz, $^2J_{PP}$ = 102.5 Hz, 1P), 99.3 (d of d, $^2J_{PP}$ = 102.5 Hz, $^4J_{PP}$ = 19.0 Hz, 1P), 104.0 (d of d, $^2J_{PP}$ = 116.5 Hz, $^4J_{PP}$ = 19.0 Hz, 1P); **18a**:**18b** = 2:1. **18a/b** could not be isolated by chromatography or crystallization techniques.

Reaction using a $PhPCl_2$:**8** ratio of <2 yielded minor resonances assignable to one diastereomer of the highly reactive intermediate **17**. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 103.2 (d, $^2J_{PP}$ = 118.5 Hz, 1P), 81.2 (d, 1P). Attempts to characterize **17** were unsuccessful.

Reaction of 10 with $PhPCl_2$ To Form $C_6H_4(MeN)[NP(Cl)Ph]P(S)Ph$ (19). A toluene solution (10 mL) of **10** (0.5460 g, 2.1 mmol) was added dropwise to a toluene solution (30 mL) of $PhPCl_2$ (0.26 mL, 2.1 mmol) and Et_3N (0.31 mL, 2.2 mmol) at 0 °C. After 5 min, the $^{31}P\{^1H\}$ NMR spectrum showed resonances attributable to diastereomers of **19a** and **19b** (**19a**:**19b** = 5:1). Et_3NHCl was removed by filtration. **19a**: δ 103.0 (d, $^2J_{PP}$ = 115 Hz, 1P), 84.7 (d, 1P). **19b**: δ 99.9 (d, $^2J_{PP}$ = 103 Hz, 1P), 84.5 (d, 1P). MS (EI$^+$): M$^+$ m/e 402.

Addition of excess S_8 to a **14a/14b** (1:1) mixture in toluene at 25 °C yielded **19a/19b** (**19a**:**19b** mole ratio = 5:1).

Reaction of 19a/19b with nor·Mo(CO)$_4$ To Form $C_6H_4(MeN)[NP(Cl)Ph]P(S)PhMo(CO)_4$ (20a/20b). Excess nor·Mo(CO)$_4$ was added to a **19a/19b** (5:1 diastereomer mixture) reaction solution (toluene solvent), and the mixture was stirred for 5 min. The $^{31}P\{^1H\}$ NMR spectrum exhibited resonances attributable to both diastereomers of **20**: **20a** (~83% spectral area), δ 135.7 (d, $^2J_{PP}$ = 106.7 Hz, 1P), 80.7 (d, 1P); **20b** (~17% spectral area), δ 142.0 (d, $^2J_{PP}$ = 101 Hz, 1P), 79.0 (d, area 1). X-ray-quality crystals of **20a** were obtained from CH_2Cl_2/hexanes. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 135.7 (d, $^2J_{PP}$ = 106.7 Hz, 1P), 80.7 (d, 1P). ^1H NMR (toluene-d_8): δ 1.8 (d, 3H, $^3J_{PH}$ = 10.5 Hz), 5.5–7.4 (m, 14H). MS (EI$^+$): M$^+$ m/e 612. IR (cm^{-1}): 2032 (s), 1928 (b), 1870 (m), 1482 (s), 1203 (s), 920 (s), 737 (s). Mp: dec >160 °C.

X-ray Analyses. (A) $[C_6H_4(N)(MeN)PPh]_2PPh$ (15a). Crystals of **15a** were obtained by crystallization from toluene. Data collection and structure solution details are summarized in Table 1, and atomic coordinates are given in Table 2. The structure was solved by direct methods and refined by least-squares calculations treating non-hydrogen atoms anisotropically.[20] Hydrogen atoms were included in idealized positions and refined riding on the atoms to which they were attached. Complete listings of data collection and structure solution details, H atom coordinates, structural parameters, and least-squares planes and interplane dihedral angles are given in the supplementary material.

Table 2. Atomic Coordinates[a] (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[C_6H_4(N)(MeN)PPh]_2PPh$ (**15a**)

atom	x	y	z	U_{eq}[b]
P(1)	3338(2)	1476(1)	7367(1)	58(1)
P(2)	3168(1)	4057(1)	6855(1)	49(1)
P(3)	393(1)	3295(1)	6966(1)	50(1)
N(1)	32373(5)	949(3)	6253(4)	57(2)
N(2)	3644(4)	2778(3)	6481(3)	47(2)
N(3)	1448(4)	4259(3)	6988(3)	46(2)
N(4)	−609(4)	4385(3)	6435(4)	51(2)
C(1)	2458(6)	37(5)	6375(6)	80(3)
C(2)	3800(5)	1638(4)	5192(5)	50(3)
C(3)	4028(5)	2692(4)	5310(5)	48(2)
C(4)	4551(5)	3490(5)	4370(5)	55(3)
C(5)	4856(6)	3232(5)	3289(5)	64(3)
C(6)	4605(6)	2214(6)	3174(5)	70(3)
C(7)	4086(5)	1403(5)	4132(6)	59(3)
C(8)	826(5)	5376(4)	6831(4)	47(2)
C(9)	−345(5)	5426(5)	6515(4)	49(2)
C(10)	−1066(6)	6455(5)	6268(5)	59(3)
C(11)	−592(7)	7409(5)	6364(5)	71(3)
C(12)	579(7)	7344(5)	6663(5)	67(3)
C(13)	1294(6)	6312(4)	6922(5)	58(3)
C(14)	−1822(6)	4196(5)	6201(5)	70(3)
C(15)	5079(6)	984(5)	7425(5)	61(3)
C(16)	6284(7)	1376(5)	6651(6)	75(3)
C(17)	7553(8)	943(7)	6747(8)	97(5)
C(18)	7639(11)	115(8)	7653(10)	122(7)
C(19)	6474(13)	−284(7)	8450(9)	114(6)
C(20)	5194(9)	158(6)	8343(6)	84(4)
C(21)	3181(6)	3681(4)	8328(5)	50(2)
C(22)	4420(7)	3490(6)	8533(7)	87(4)
C(23)	4474(9)	3312(7)	9642(8)	111(5)
C(24)	3333(10)	3342(6)	10528(7)	99(5)
C(25)	2098(8)	3511(5)	10344(6)	79(4)
C(26)	2013(6)	3695(5)	9257(5)	65(3)
C(27)	−657(5)	2928(5)	8467(4)	50(2)
C(28)	−599(7)	1834(6)	9001(6)	83(3)
C(29)	−1315(8)	1500(6)	10141(6)	111(4)
C(30)	−2079(7)	2274(8)	10752(6)	95(4)
C(31)	−2189(6)	3365(6)	10244(6)	77(3)
C(32)	−1495(6)	3696(5)	9109(5)	69(3)

[a] Atoms have occupanices of 1.0. [b] Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(B) $C_6H_4(MeN)[NP(Cl)Ph]P(S)PhMo(CO)_4$ (20a). Crystals of **20a** were obtained by crystallization from CH_2Cl_2/hexanes. Data collection and structure solution details are summarized in Table 1, atomic coordinates are given in Table 3. The structure was solved by direct methods and refined by least-squares calculations treating non-hydrogen atoms anisotropically.[20] Hydrogen atoms were included in idealized positions and refined riding on the atoms to which they were attached. Complete listings of data collection and structure solution details, H atom coordinates, structural parameters, and least-squares planes and interplane dihedral angles are given in the supplementary material.

Results and Discussion

Reactions of phosphadiazoles **7–10** with $PhPCl_2$, **7** and **9** with $PhP(NEt_2)Cl$, and **7** and **8** with Ph_2PCl yield di- and/or triphosphazane products. The **7–10**/$PhPCl_2$ reaction products provide information about di- and triphosphazane stereochemistry as expressed in amine–chlorophosphine condensations; the **7**/$PhP(NEt_2)Cl$ reaction provides stereochemical information about di- and triphosphazanes formed through transaminative processes.[21] All reactions are of interest for the information they provide about skeletally stabilized extended phosphazane formation.

Phosph(III)adiazole **7** reacts rapidly with both $PhPCl_2$ and Ph_2PCl (eq 3) at room temperature to form the products of amine–

(20) Sheldrick, G. M. *SHELXTL PLUS: A Program for Crystal Structure Determination*, Version 4.1; Siemens Analytical Instruments: Madison, WI, 1990; performed on a Micro VAX II.

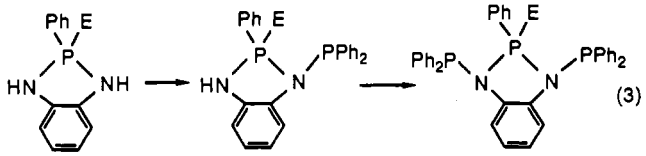
(21) (a) Keat, R. *Top. Curr. Chem.* **1983**, *102*, 89. (b) Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 101.

Table 3. Atomic Coordinates[a] (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for $C_6H_4(MeN)[NP(Cl)Ph]P(S)PhMo(CO)_4$ (**20a**)

atom	x	y	z	U_{eq}[b]
Mo(1)	1394(1)	2072(1)	7553(1)	48(1)
Cl(1)	3346(1)	161(1)	8889(1)	76(1)
S(1)	1242(1)	4011(1)	8176(1)	58(1)
P(1)	1882(1)	3357(1)	9080(1)	46(1)
P(2)	3194(1)	1711(1)	8433(1)	45(1)
O(1)	-1104(2)	2546(3)	6554(1)	119(1)
O(2)	1805(2)	20(3)	6676(2)	103(1)
O(3)	-150(2)	409(2)	8309(1)	77(1)
O(4)	2972(2)	3330(3)	6584(1)	106(1)
N(1)	2566(2)	4219(2)	9690(1)	59(1)
N(2)	3159(2)	2565(2)	9114(1)	48(1)
C(1)	1947(3)	5147(3)	9939(2)	79(1)
C(2)	3713(2)	3793(3)	10031(1)	58(1)
C(3)	4428(3)	4212(3)	10625(2)	80(1)
C(4)	5516(3)	3652(4)	10875(2)	92(1)
C(5)	5860(3)	2737(3)	10562(2)	84(1)
C(6)	5146(3)	2287(3)	9960(2)	66(1)
C(7)	4058(2)	2860(2)	9707(1)	52(1)
C(8)	4721(2)	1919(3)	8245(1)	57(1)
C(9)	5511(3)	1052(3)	8146(2)	82(1)
C(10)	6567(3)	1313(5)	7900(2)	116(2)
C(11)	6842(4)	2364(7)	7746(2)	127(3)
C(12)	6076(3)	3209(5)	7853(2)	113(2)
C(13)	5018(3)	3003(3)	8102(2)	79(1)
C(14)	-189(2)	2400(3)	6901(1)	70(1)
C(15)	1646(2)	761(3)	7010(2)	67(1)
C(16)	402(2)	1054(3)	8072(1)	54(1)
C(17)	2407(3)	2910(3)	6945(2)	68(1)
C(18)	748(2)	2588(2)	9435(1)	50(1)
C(19)	1147(3)	1891(3)	9992(1)	63(1)
C(20)	304(3)	1340(3)	10296(2)	78(1)
C(21)	-935(3)	1474(3)	10053(2)	76(1)
C(22)	-1336(3)	2162(3)	9505(2)	73(1)
C(23)	-504(2)	2741(2)	9189(2)	59(1)

[a] Atoms have occupancies of 1.0. [b] Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

chlorophosphine condensation. Irrespective of reactant ratios,



(3)

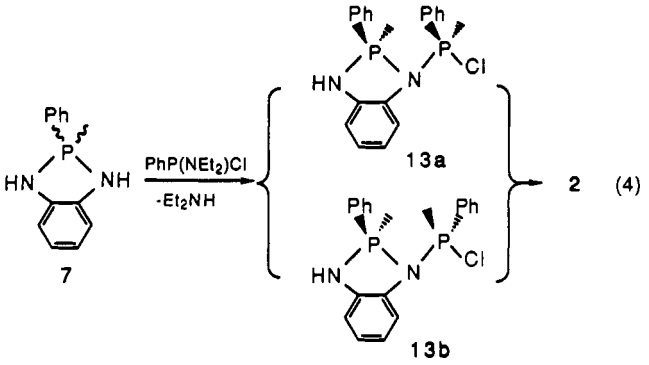
7; E = LP
8; E = S

11; E = LP

12; E = LP
16; E = S

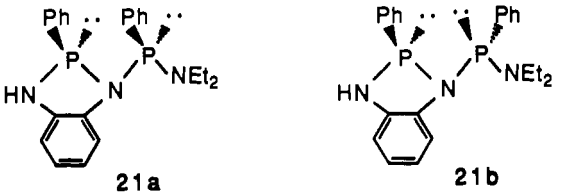
reactions proceed rapidly beyond diphosphazanes. The $7/Ph_2PCl$ reaction yields triphosphophazane **12**; only small equal-area doublet resonances attributable to intermediate **11** were seen. Only when the halophosphine is added to excess **7** is **11** detectable. Compound **12** shows a characteristic AX_2[19] $^{31}P\{^1H\}$ NMR spectrum; the Ph_2P resonance at δ 41.8 is in the expected region.[22] The phosphadiazole resonance at δ 96.5 is in the region of those (δ 78.6 and 91.6) observed for phosph(III)adiazoles **7** and **9**.[1c,16] The $7/PhPCl_2$ reactions are also very facile and proceed quickly to form the skeletally stabilized phosphazanes (**1**, **2**) reported earlier.[5] These reactions often show appreciable quantities of competing oxidation products and thus are complex reaction mixtures.

In contrast to its reactions with Ph_2PCl or $PhPCl_2$, **7** reacts with the amino(chloro)phosphine $PhP(NEt_2)Cl$ more slowly and, when the reaction is carried out in in the absence of Et_3N or under vacuum to remove Et_2NH, via a transaminative process. Thus at 25 °C, **7** and $PhP(NEt_2)Cl$ react slowly in toluene (eq 4) to form a mixture which exhibits two pairs of equal-area ^{31}P NMR doublet resonances at δ 114.3 and 90.6 ($^2J_{PP}$ = 170.0 Hz) and δ 117.3 and 89.0 ($^2J_{PP}$ = 80.0 Hz) attributable to a 1:1 mixture of diastereomers **13a** and **13b**. Little evidence is seen for



(4)

competitive formation of diphosphazanes such as **21a** or **21b** that would result from amine–chlorophosphine condensation. Com-



pounds **13a**/**13b** could not be isolated; they are highly reactive and quickly undergo condensation to cyclophosphazanes (**2**). The P–Cl bond of $PhP(NEt_2)Cl$ greatly enhances the rate at which the P–NEt_2 unit undergoes transamination. The $7/PhP(NEt_2)_2$ reaction occurs very slowly only upon heating above 90 °C and then not cleanly. Only when $7/PhP(NEt_2)Cl$ reactions are carried out in the presence of Et_3N are resonances in complex reaction mixtures observed which can be tentatively assigned to phosphazane products such as **21a**/**21b**. Importantly, even though the chlorodiphosphazanes **13a** and **13b** form via transaminative processes, they form in a 1:1 ratio as do the chlorodiphosphazanes **14** and as does **5**, which results from the $PhPCl_2/i\text{-}PrNH_2$ reaction.[10] No diastereoselection of the chlorodiphosphazanes is seen in any case.

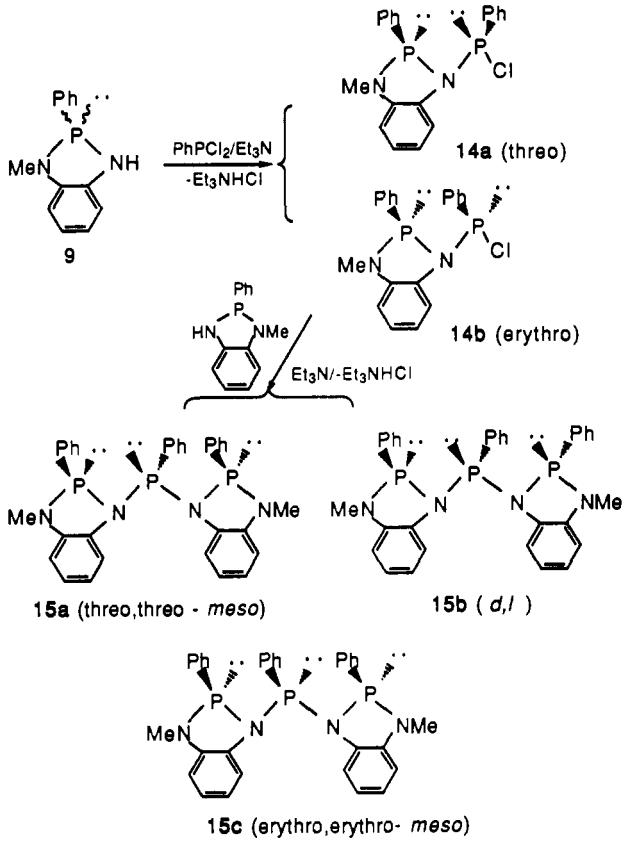
Since we were unable to isolate di- and triphosphazane intermediates from $7/PhPCl_2$ or $7/PhP(Et_2N)Cl$ reactions by fractional crystallization or column chromatography, reactivity of the *N*-Me-substituted analog, **9**, was examined (Scheme 1). With **9**, extended phosphazane formation is blocked and products are limited to di- and triphosphazanes. Thus addition of $PhPCl_2$ to **9** and Et_3N in toluene proceeds cleanly to form two isomers of triphosphazane **15**, **15a** and **15b**. Upon combination of reagents, the ^{31}P NMR spectrum showed an AX_2 doublet and triplet (**15a**) and an AMX set of three equal-area resonances (**15b**) in a **15a**:**15b** ratio of 5:1. Only with the opposite order of addition, that of **9** to $PhPCl_2$ and Et_3N, were small quantities of the intermediate diphosphazanes **14a** and **14b** seen, as shown by the two pairs of equal-area coupled ^{31}P NMR doublets at δ 115.0 and 101.0 (**14a**) and δ 113.0 and 101.5 (**14b**). ^{31}P NMR and MS data characterize **14a**/**14b** unequivocally; however, they could not be obtained in high yield from this reaction. Compounds **14a**/**14b** could be formed in high yield, >90% conversion, from the addition of $o\text{-}C_6H_4(MeNH)(NH_2)$ to 2 equiv of $PhPCl_2$ and excess Et_3N (>3 equiv) and also show a 1:1 diastereomer ratio.

Triphosphazane **15** can exist in three diastereomeric forms:[23] *threo,threo-meso* (**15a**), *d,l* (**15b**), and *erythro,erythro-meso* (**15c**). Although the AX_2 ^{31}P NMR spectral pattern shows clearly

(22) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *Topics in Phosphorus Chemistry*; Interscience: New York, 1967; Vol. 5.

(23) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985.

Scheme 1



that **15a** is one of the two possible meso isomers, a single-crystal X-ray analysis was needed in order to determine the absolute configuration. The structure of **15** is shown in Figure 1, and selected bond distance and angle data are listed in Table 4. Compound **15a** is the *threo,threo-meso* isomer; the structure consists of two *N*-Me-substituted phosphadiazoles bonded to a bridging PhP group. When the molecule is rotated such that the *o*-C_6H_4 groups are aligned downward, the phosphadiazole phenyl groups are on one side and the bridging PhP phenyl group is on the opposite side of the triphosphazane skeleton. The P–N distances are typical of those seen in other phosph(III)adiazole-containing phosphazanes;[1-7,24,25] the mean phosphadiazole ring P–N distances of 1.730 Å are slightly longer than the mean bridging P–N distances of 1.710 Å. The angles around P and N atoms in the system are also typical; however, the overall molecular conformation is of interest. The phosphazane skeleton is far from linear but rather highly twisted in the direction of a larger phosphazane ring. In fact, the P and N atom relative positions are suprisingly close to where they would be in the skeletally stabilized cyclotetraphosphazane ring of $[C_6H_4N_2(PhP)_2]_2$ (**2**, R = Ph).[5] Whether this triphosphazane conformation is analogous to that of an intermediate which might precede formation of **2** in the $PhPCl_2/1,2\text{-}(NH_2)_2C_6H_4$ reaction is unclear. Studies of this latter reaction mechanism and the role intermediate conformation and configuration selection might have in the final product formation are in progress.

Examination of the phosph(III)adiazole/$PhPCl_2$ or phos(III)-adiazole/$PhP(NEt_2)Cl$ reaction product stereochemistry indicates that, as with the acyclic diphosphazanes (**5**, eq 2), no stereoselectivity is shown in formation of the chlorodiphosphazane intermediates by either amine–chlorophosphine or transamination reactions. Both reactions yield chlorodiphosphazanes in 1:1 ratios.

(24) Malavaud, C.; N'Gando M'Pondo, T.; Lopez, L.; Barrans, J.; Legros, J.-P. *Can. J. Chem.* **1984**, *62*, 43.
(25) Karaghiosoff, K.; Klehr, H.; Schmidpeter, A. *Chem. Ber.* **1986**, *119*, 410.

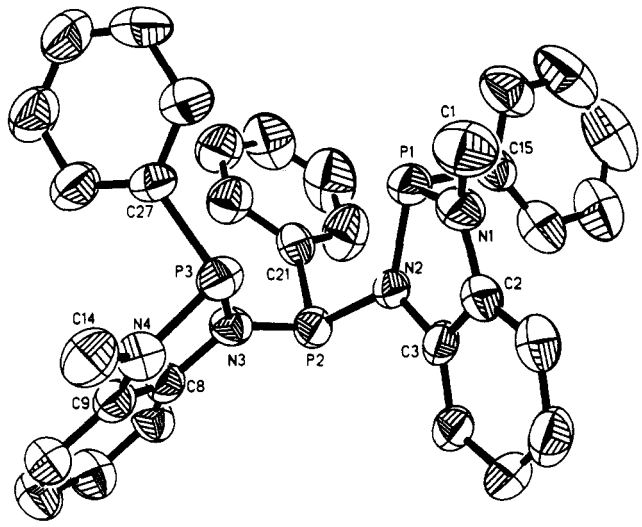


Figure 1. Structure and numbering scheme for $[C_6H_4(N)(MeN)PPh]_2$-PPh (**15a**). Thermal ellipsoids are shown at the 50% probability level.

Table 4. Selected Structural Parameters for $[C_6H_4(N)(MeN)PPh]_2PPh$ (**15a**)

(a) Bond Lengths (Å)

P(1)–N(1)	1.710(6)	P(1)–N(2)	1.738(4)
P(1)–C(15)	1.834(7)	P(2)–N(2)	1.705(4)
P(2)–N(3)	1.718(5)	P(2)–C(21)	1.821(6)
P(3)–N(3)	1.745(5)	P(3)–N(4)	1.718(4)
P(3)–C(27)	1.839(5)	N(1)–C(1)	1.458(8)
N(1)–C(2)	1.397(6)	N(2)–C(3)	1.428(7)
N(3)–C(8)	1.427(6)	N(4)–C(9)	1.385(8)
N(4)–C(14)	1.448(9)	C(2)–C(3)	1.406(8)
C(8)–C(9)	1.388(9)		

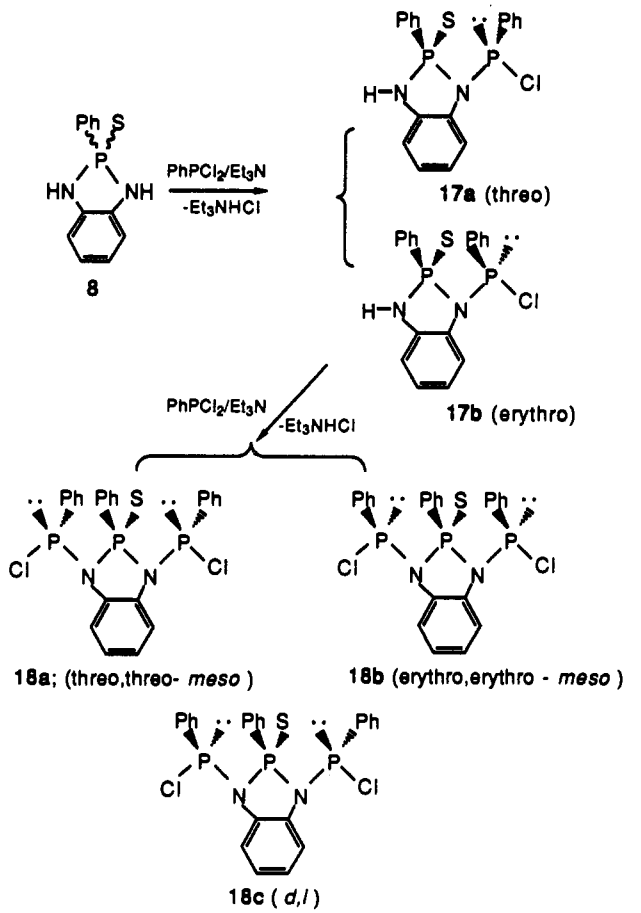
(b) Angles (deg)

N(1)–P(1)–N(2)	90.1(2)	N(1)–P(1)–C(15)	102.4(3)
N(2)–P(1)–C(15)	99.9(2)	N(2)–P(2)–N(3)	103.4(2)
N(2)–P(2)–C(21)	99.6(2)	N(3)–P(2)–C(21)	103.2(2)
N(3)–P(3)–N(4)	89.2(2)	N(3)–P(3)–C(27)	103.4(3)
N(4)–P(3)–C(27)	102.1(2)	P(1)–N(1)–C(1)	124.3(4)
P(1)–N(1)–C(2)	113.3(4)	C(1)–N(1)–C(2)	120.8(6)
P(1)–N(2)–P(2)	127.3(2)	P(1)–N(2)–C(3)	111.0(3)
P(2)–N(2)–C(3)	119.8(3)	P(2)–N(3)–P(3)	127.9(2)
P(2)–N(3)–C(8)	118.8(4)	P(3)–N(3)–C(8)	111.5(4)
P(3)–N(4)–C(9)	113.7(4)	P(3)–N(4)–C(14)	121.5(4)
C(9)–N(4)–C(14)	123.1(4)	N(1)–C(2)–C(3)	111.4(5)
N(1)–C(2)–C(7)	128.4(5)	N(2)–C(3)–C(4)	127.9(5)
N(2)–C(3)–C(2)	111.5(4)	N(3)–C(8)–C(9)	111.3(5)
N(3)–C(8)–C(13)	126.9(5)	N(4)–C(9)–C(10)	127.6(6)
N(4)–C(9)–C(8)	112.2(5)	P(1)–C(15)–C(16)	126.1(5)
P(1)–C(15)–C(20)	116.9(5)	P(2)–C(21)–C(26)	123.7(5)
P(2)–C(21)–C(22)	118.5(4)	P(3)–C(27)–C(28)	118.1(4)
P(3)–C(27)–C(32)	124.5(4)		

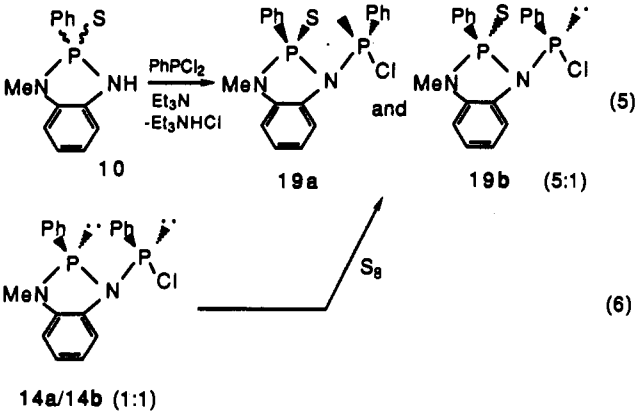
In addition, as in the acyclic system, stereochemical selection occurs only at the time of chlorodiphosphazane terminal P–Cl bond amination. The 1:1 **14a** (*threo*):**14b** (*erythro*) mixture yields mainly the *threo,threo-meso* isomer, **15a**. Minor quanitites of the *d,l* diasteteromer (**15b**) are seen; no *erythro,erythro-meso* (**15c**) was detected. Unlike the case of the acyclic phosphazanes, which form predominantly as *erythro* amination products (eq 2), the order of stereoselection in formation of the skeletally substituted phosphazanes is reversed.

Reactions of the phospha(V)diazoles **8** and **10** with $PhPCl_2$ were examined to determine if under phosphadiazole–chlorophosphine condensation stereoselective formation of λ^4–λ^3 di- or λ^3–λ^4–λ^3 triphosphazanes might occur. Reactions of **8** with Ph_2PCl yield products useful for spectral correlations. In all cases, the phosphadiazole–chlorophosphine reactions were conducted in the presence of Et_3N to remove HCl. Reactions of **8** and **10** are cleaner than those of the analogous P(III) compounds **7** and **9**. However, the **8**/Ph_2PCl and **8**/$PhPCl_2$ reactions proceed rapidly to form three-phosphorus products, **16** in eq 3 and **18** in

Scheme 2



Scheme 3



Scheme 2. Only traces of a diphosphorus product could be seen in the **8**/$PhPCl_2$ reaction. When **8** was maintained in excess, small doublet resonances at δ 103.2 and 81.2 attributable to one isomer of $C_6H_4(NH)[PN(Cl)Ph]P(S)Ph$ (**17**) were seen; however, yields were always very low. Compounds **17** and **18** are highly reactive; thus we were unable to isolate and characterize them out of their reaction solutions.

Since we were unable to obtain unambiguous structural characterization of **17** and **18** directly, we sought stereochemical information from reactions of $PhPCl_2$ with the *N*-Me-blocked phosphadiazole, **10** (Scheme 3). Slow addition of **10** to $PhPCl_2$ and Et_3N in toluene at 0 °C yields nearly quantitatively the λ^4–λ^3 chlorodiphosphazane diastereomers **19a** and **19b**, typically in an ca. 5:1 ratio. Even with excess **10**, the reaction showed little tendency to form a triphosphazane. The two diastereomers exhibit the expected pairs of doublet resonances; the low-field resonances at δ 103.0 and 99.9 and the higher-field resonances at δ 84.7 and 84.5 are in the regions expected for NP(Ph)Cl[11,22] and phosph(V)adiazole[1–8,24] type phosphorus atoms.

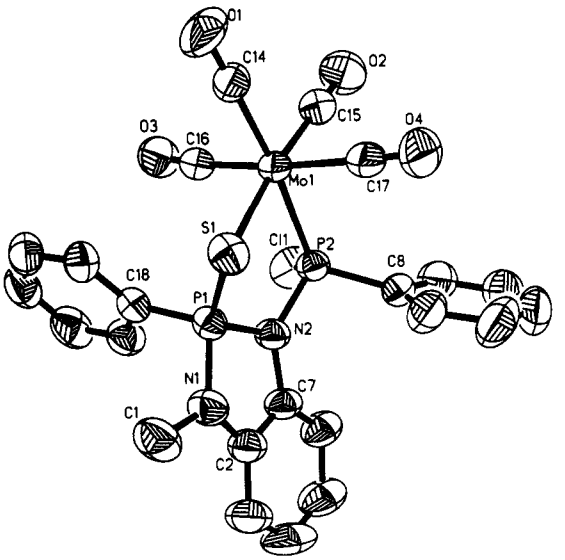


Figure 2. Structure and numbering scheme for $C_6H_4(MeN)[NP(Cl)Ph]P(S)PhMo(CO)_4$ (**20a**). Thermal ellipsoids are shown at the 50% probability level.

Attempts to were made to isolate and crystallize **19a** and/or **19b** for X-ray crystallographic determination of their absolute configurations and to determine which of the two possible diastereomers, *erythro* or *threo*, is formed. Although, crystals of either isomer adequate for analysis were not obtained, the **19a**/**19b** mixture reacted readily with nor·$Mo(CO)_4$ to form crystallizable complexes **20a**/**20b**. The **19a**:**19b** isomer ratio is typically 5:1; within experimental error the complexes **20a**/**20b** are formed in the same ratio. The major isomer **20a**, which results from $Mo(CO)_4$ complexation of **19a**, was subjected to X-ray analysis.

The structure of **20a** is shown in Figure 2, and selected structural data are listed in Table 5. The complex consists of the chlorodiphosphazane coordinated through a sulfur and the phosphorus lone pair to cis positions of the $Mo(CO)_4$ group. The chlorodiphosphazane is the *threo* diastereomer. Complexes which contain phosphorus lone-pair and phosphine sulfide sulfur (P=S) donating ligands are rare; therefore, systems with which to compare structural parameters are limited. However, general structural features such as angles around Mo, P–N bond distances, and phosphazane skeletal angles are unexceptional and consistent with those expected.[26,27] The Mo–P bond distance of 2.427 Å is in the range expected for phosphine–Mo(0) bonds.[26–28] The five-membered MoPNPS ring is highly twisted, the atom deviations from a least-squares plane being as follows: Mo, –0.24 Å; P, 0.18 Å, N, 0.09 Å; P, –0.39 Å, S, 0.36 Å.

Assuming that $Mo(CO)_4$ moiety coordination to **19a**/**b** occurs without perturbation of the basic *erythro*:*threo* isomer ratio, we conclude that the **10**/$PhPCl_2$ reaction is diastereoselective for formation of the *threo* isomer. However, even though *threo* diastereomer formation is preferred in the **10**/$PhPCl_2$ reaction (Scheme 3), it is not immediately clear whether this is a thermodynamic or kinetic result. Heating **19a**/**19b** at 80 °C causes no change in isomer ratio. However, reaction of a 1:1

(26) (a) Tarassoli, A.; Chen, H.-J.; Thompson, M. L.; Allured, V. S.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1986**, *25*, 4152. (b) McAuliffe, C. A.; Levanson, W. *Phosphine, Arsine, and Stibine Complexes of the Transition Metal Elements*; Elsevier: Amsterdam, 1979.
(27) (a) Brown, G. M.; Finholt, J. E.; King, R. B.; Bibber, J. W.; Kim, J. H. *Inorg. Chem.* **1982**, *21*, 3790. (b) Brown, G. M.; Finholt, J. E.; King, R. B.; Lee, T. W. *J. Am. Chem. Soc.* **1981**, *103*, 5249.
(28) Socol, S. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 88.

Table 5. Selected Structural Parameters for $C_6H_4(MeN)[NP(Cl)Ph]P(S)PhMo(CO)_4$ (**20a**)

(a) Bond Lengths (Å)

Mo(1)–S(1)	2.646(1)	Mo(1)–P(2)	2.427(1)
Mo(1)–C(14)	2.012(3)	Mo(1)–C(15)	1.945(3)
Mo(1)–C(16)	2.031(3)	Mo(1)–C(17)	2.040(3)
Cl(1)–P(2)	2.056(1)	S(1)–P(1)	1.948(1)
P(1)–N(1)	1.656(2)	P(1)–N(2)	1.693(2)
P(1)–C(18)	1.795(3)	P(2)–N(2)	1.687(2)
P(2)–C(8)	1.809(3)	O(1)–C(14)	1.126(3)
O(2)–C(15)	1.136(5)	O(3)–C(16)	1.134(4)
O(4)–C(17)	1.140(4)	N(1)–C(1)	1.438(4)
N(1)–C(2)	1.419(3)	N(2)–C(7)	1.430(3)
C(2)–C(7)	1.373(4)		

(b) Angles (deg)

S(1)–Mo(1)–P(2)	86.6(1)	S(1)–Mo(1)–C(14)	90.1(1)
P(2)–Mo(1)–C(14)	174.3(1)	S(1)–Mo(1)–C(15)	171.7(1)
P(2)–Mo(1)–C(15)	93.7(1)	C(14)–Mo(1)–C(15)	90.3(1)
S(1)–Mo(1)–C(16)	102.3(1)	P(2)–Mo(1)–C(16)	89.1(1)
C(14)–Mo(1)–C(16)	87.1(1)	C(15)–Mo(1)–C(16)	86.1(1)
S(1)–Mo(1)–C(17)	85.6(1)	P(2)–Mo(1)–C(17)	92.1(1)
C(14)–Mo(1)–C(17)	92.3(1)	C(15)–Mo(1)–C(17)	86.1(1)
C(16)–Mo(1)–C(17)	172.1(1)	Mo(1)–S(1)–P(1)	91.3(1)
S(1)–P(1)–N(1)	116.7(1)	S(1)–P(1)–N(2)	115.3(1)
N(1)–P(1)–N(2)	92.9(1)	S(1)–P(1)–C(18)	113.1(1)
N(1)–P(1)–C(18)	107.6(1)	N(2)–P(1)–C(18)	109.4(1)
Mo(1)–P(2)–Cl(1)	117.6(1)	Mo(1)–P(2)–N(2)	108.8(1)
Cl(1)–P(2)–N(2)	102.5(1)	Mo(1)–P(2)–C(8)	120.4(1)
Cl(1)–P(2)–C(8)	101.9(1)	N(2)–P(2)–C(8)	103.4(1)
P(1)–N(1)–C(1)	123.0(2)	P(1)–N(1)–C(2)	111.7(2)
C(1)–N(1)–C(2)	124.0(2)	P(1)–N(2)–P(2)	116.5(1)
P(1)–N(2)–C(7)	110.3(2)	P(2)–N(2)–C(7)	132.9(2)
N(1)–C(2)–C(3)	126.5(3)	N(1)–C(2)–C(7)	112.0(2)
C(5)–C(6)–C(7)	115.4(3)	N(2)–C(7)–C(2)	111.4(2)
N(2)–C(7)–C(6)	126.6(2)	C(2)–C(7)–C(6)	122.0(2)
P(2)–C(8)–C(9)	123.8(2)	P(2)–C(8)–C(13)	115.8 (2)
Mo(1)–C(14)–O(1)	176.5(3)	Mo(1)–C(15)–O(2)	177.6(3)
Mo(1)–C(16)–O(3)	173.0(2)	Mo(1)–C(17)–O(4)	176.4(3)
P(1)–C(18)–C(19)	118.1(2)	P(1)–C(18)–C(23)	121.2(2)

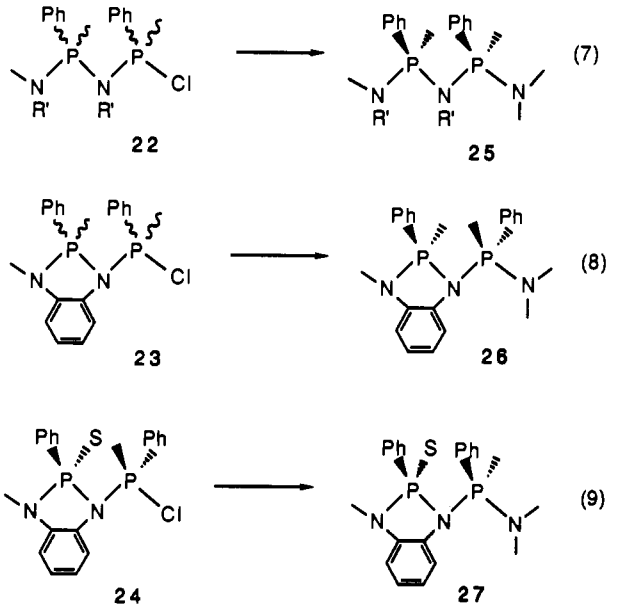
14a:**14b** diastereomer mixture with S_8 (eq 6, Scheme 3) yields **19a**/**19b** quantitatively in a 5:1 ratio. Since **19a** and **19b** in the same ratio (5:1) are obtained from two quite different reactions, we conclude the 5:1 ratio is the result of thermodynamic effects and represents the equilibrium isomer mixture for the system at 25 °C.

Because *threo* diphosphazane **19a** is the predominant product of **10**/$PhPCl_2$ reaction, we conclude that the isomer of **17** observed in the **8**/$PhPCl_2$ reaction (Scheme 2) might also be the *threo* form, i.e. **17a**. The *erythro* **17b** is not seen; however, since the diphosphazane concentration is always low and its existence fleeting, it may be present but below our detection limits.

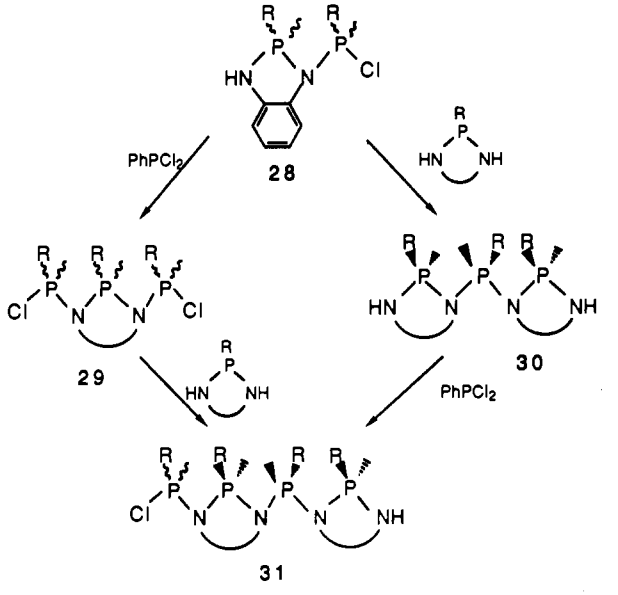
Stereochemistry of the λ^3–λ^4–λ^3 triphosphazane **18** (Scheme 2) is a more complex issue. The **8**/$PhPCl_2$ reaction can in principle yield three diastereomers: *threo,threo-meso* (**18a**), *erythro,-erythro-meso* (**18b**), and *d,l* (**18c**). The ^{31}P NMR spectrum of the reaction mixture shows an AX_2 triplet and doublet pattern at δ 88.0 and 102.5 (J = 112 Hz), respectively, and an AMX pattern of coupled, equal-area resonances at δ 86.6, 102.5, and 99.3; hence, in fact, only the *d,l* and one of the *meso* forms are seen. The *d,l* and *meso* forms are present in a 1:2 ratio. Assuming *threo*-forming stereoselection dominates formation of the chlorodiphosphazane intermediate, i.e. **17a**, as is also seen to be the case with **19a**, we might expect that the triphosphazane isomer which dominates is **18a**, the *threo,threo-meso* form. Isomer **18c** would result from the *erythro*-selection mode which produces the *d,l* isomer. Of note, *threo* selection is less favored in formation of **18** than in the formation of **17**. Since essentially no **17b** is seen in the diphosphazane formation step, it is not suprising that the *erythro,erythro-meso* form (**18b**) is absent as a reaction product.

Our studies of the skeletally stabilized chlorodiphosphazane formation and chlorodiphosphazane amination reactions show interesting differences and similarities (Scheme 4). Formation

Scheme 4



Scheme 5



of λ^3–λ^3 chlorodiphosphazanes of both the acyclic (**22**) and the skeletally stabilized (**23**) types occurs with no detectable diastereomer preference. In contrast, the λ^4–λ^3 chlorodiphosphazanes (**24**) occur with an appreciable degree of *threo* stereoselection. Further, although amination of both **22** and **23** shows stereoselection, it occurs in opposite fashion; amination of **22** favors *erythro* **25** whereas amination of **23** favors the *threo* **26** product. Since products of the λ^4–λ^3 chlorodiphoshphazane **24** amination have not yet been obtained, stereoselection in the formation of **27** remains undetermined; however, because selectivity is shown already in the formation of **24**, it seems likely that it will be shown in the next amination step as well.

Although it is not yet understood why acyclic chlorophosph(III)azane (**5**) amination stereoselection is opposite that of a skeletally substituted chlorodiphosphazane (e.g., to form **15a**), the result suggests what might be expected in the formation of more highly extended skeletally stabilized phosphazanes (Scheme 5). The phosphadiazole/$PhPCl_2$ reaction likely first yields a chlorodiphosphazane **28**, which can extend the phosphazane chain by reaction in two ways, either by adding $PhPCl_2$ to the phosphadiazole N–H bond (**29**) or by adding a phosphadiazole

to the P–Cl bond (**30**). If we assume that, as in systems studied above, the addition of a $PhPCl_2$ unit occurs with little or no stereoselection, it will be only the aminations by phosphadiazole which result in stereoselection and in doing so they will preferentially orient the phosphorus R groups in an alternating fashion (e.g., **31**). As the process continues, to the extent this occurs in a condensation chain extension process, the chain extension might be expected to favor formation of a syndiotactic polymer.

Although the present study has extended our understanding of stereselection modes in phosphazane formation reactions, the generality of stereoselection and the origin of the selectivity remain to be understood and quantified. Studies along these lines are in progress and will be reported later.

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Supplementary Material Available: Tables giving crystal data and details of the crystal structure determinations, anisotropic thermal parameters, bond lengths and angles, hydrogen atom locations, and least-squares planes and dihedral angles for **15a** and **20a** (22 pages). Ordering information is given on any current masthead page.