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Synthesis, Characterization, and Solution Properties of Skeletally Stabilized Triphosphazanes

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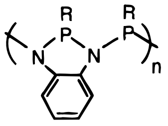
The new skeletally stabilized dichlorotriphosphazanes $C_6H_4N_2(PhPCl)_2PPh$ (**5**) and $C_6H_4N_2(MePCl)_2PMe$ (**6**) have been prepared from reactions between $PhPCl_2$ or $MePCl_2$ and 1,2-$(NH_2)_2C_6H_4$ or 1,2-$(Me_3SiNH)_2C_6H_4$, respectively. Reaction of $PhPCl_2$ with the phosphadiazole $C_2H_4(Me_3SiN)_2PPh$ yields triphosphazane $C_2H_4N_2(PhPCl)_2PPh$ (**8**). Compounds **5**, **6**, and **8** form as mixtures of three diastereomers; characterization is based on spectral data and derivatization of **5** and **8** to the amino and thio(amino) triphosphazanes $C_6H_4N_2[PhP(NH^iPr)]_2PPh$ (**7**) and $C_2H_4N_2[PhP(S)NEt_2]_2PPh$ (**10**). The ^{31}P NMR spectra of **5** and **6** in solution have been measured as a function of temperature and solvent donor and dielectric strength. The solution properties of the dichlorotriphosphazanes and the implications of these on subsequent reaction chemistry are discussed.

Introduction

The introduction of a bridging group, e.g., an *o*-phenylene ring, between adjacent nitrogen atoms in a phosphazane chain has allowed the synthesis of acyclic and cyclic oligomers of the general form **1**.[1−6] As part of our effort to find efficient routes to these new molecules, especially the cyclooligomers (e.g., $n = 2, 3$), we wished to obtain two- and three-phosphorus synthons which in subsequent reactions might (i) form known rings in improved yields and also (ii) lead to new ring systems. Of particular interest for this are difunctional triphosphazanes (**2**, X = halogen) which can be envisaged to react at both *exo* −P(R)X units. To this end we have now studied reactions by which these compounds can be prepared. In addition, we find that they show interesting solution properties which have implications as to their participation in subsequent reactions. Our results are summarized below.



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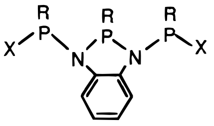

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Experimental Section

Apparatus and Materials. Phosphorus-31 and ^1H NMR spectra were recorded with Varian VXR-300S, Bruker AM-400, and Varian Inova-500 spectrometers operating at (^{31}P, ^1H) 121.4 and 299.1, 162.0 and 400.1, and 202.6 and 500.4 MHz, respectively. ^{31}P and ^1H chemical shifts downfield from 85% H_3PO_4 (external) and Me_4Si (internal) are reported as positive ($+\delta$). Mass spectra were obtained at 70 eV with Varian MAT-CH5 or VG Analytical 7070 EQ-HF spectrometers. Mass spectral data refer to the major peak of the respective envelope. Chemical ionization (CI^+ and CI^-) was achieved using isobutane as the ionizing gas. Exact mass analyses were referenced to perfluorokerosene. Product yields were determined by integration of the ^{31}P NMR spectra of reaction mixtures. Dielectric constant measurements were made on liquid samples at 22 °C using a Model 74C-37 Boonton Electronics capacitance bridge. All manipulations were carried out using standard vacuum line, glovebag, or Schlenk techniques under dry N_2.[7] Flash chromatography was carried out according to the method of Still et al.[8] Compounds were eluted with the necessary solvent mixture under N_2 pressure, analyzed by TLC, and combined according to their R_f values.

1,2-$(NH_2)_2C_6H_4$ (Aldrich) was first recrystallized from toluene and then sublimed. Toluene, *m*-xylene and THF (over Na/benzophenone), $PhPCl_2$ (over CaH_2), $MePCl_2$, $^iPrNH_2$, Et_3N, MeCN (over P_4O_{10}) and CH_2Cl_2 (P_4O_{10}) were distilled before use. $AlCl_3$ was sublimed before use. Silica gel (EM Science) and $[Me_4N]Cl$ were used as obtained. Syntheses of 1,2-$(Me_3SiNH)_2C_6H_4$ (**3**)[9] and $C_2H_4(NSiMe_3)_2PPh$ (**4**)[9] are described elsewhere.

$C_6H_4N_2(PhPCl)_2PPh$ (5A−C). $PhPCl_2$ (2.94 mL, 21.7 mmol) in toluene (3.0 mL) was added to a stirred solution of **3** (1.8 g, 7.2 mmol) and Et_3N (2.00 mL, 14.4 mmol) in toluene (45 mL). After 170 h at 25 °C the solution was filtered, and volatile materials were removed in vacuo. ^{31}P NMR spectral analysis of the product oil showed only diastereomers **5A**/**5B**/**5C** (1.0:1.4:1.3 ratio). The **5** mixture did not

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crystallize, and isomers were not separable by chromatography (silica gel). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 117.2 (d, $^2J_{PP}$ = 104.0 Hz, 2P; PhPCl), 99.2 (t, 1P; PhP) (**5A**); δ 119.0 (d, $^2J_{PP}$ = 93.0 Hz, 2P; PhPCl), 111.4 (t, 1P; PhP) (**5B**); δ 118.1 (d, $^2J_{PP}$ = 70.8 Hz, 1P; PhPCl), 116.2 (d, $^2J_{PP}$ = 105.4 Hz, 1P; PhPCl), 98.8 (d of d, $^2J_{PP}$ = 105.4 Hz, $^2J_{PP}$ = 70.8 Hz, 1P; PhP) (**5C**). ^1H NMR (C_6D_6): δ 6.5−7.5 (complex multiplets). Anal. Calcd for $C_{24}H_{19}N_2P_3Cl_2$: C, 57.74; H, 3.84; N, 5.61; molecular mass, 498.0138 amu. Found: C, 56.97; H, 4.02; N, 5.44; molecular mass (EI$^+$, accurate mass, MS), 498.0184 amu. MS: EI$^+$, M$^+$, *m/z* 498 [$C_{24}H_{19}N_2P_3Cl_2^+$]; CI$^+$, M + 1$^+$, *m/z* 499 [$C_{24}H_{20}N_2P_3Cl_2^+$].

Alternatively, 1,2-$(NH_2)_2C_6H_4$ (0.54 g, 5.0 mmol) in acetonitrile (25 mL) was added dropwise to a solution of $PhPCl_2$ (2.0 mL, 15.0 mmol) and Et_3N (3.5 mL) in acetonitrile (2 mL). After addition was complete, the [Et_3NH]Cl that formed was filtered off. Removal of volatile materials in vacuo yielded the **5A**−**C** oil in high purity (>90%).

$C_6H_4N_2(MePCl)_2PMe$ (6A−C). $MePCl_2$ (1.60 mL, 17.9 mmol) in toluene (5 mL) was added to a solution of **3** (5.8 mmol) and Et_3N (1.62 mL, 11.6 mmol) in toluene (45 mL) at 25 °C. After 23 h, [Et_3NH]Cl was removed by filtration. $^{31}P\{^1H\}$ NMR spectral analysis of the filtrate showed **6A**−**C** (ca. 95%; **6A**:**6B**:**6C** = 1.0:1.8:3.5). Anal. Calcd for $C_9H_{13}N_2P_3Cl_2$: molecular mass, 311.9669 amu. Found: molecular mass (EI$^+$, accurate mass, MS), 311.9673 amu. MS (EI$^+$), M$^+$, *m/z* 312 [$C_9H_{13}N_2P_3Cl_2^+$]; (CI$^+$), M$^+$ + 1, *m/z* 313 [$C_9H_{14}N_2P_3Cl_2^+$]. $^{31}P\{^1H\}$ NMR (C_6D_6/toluene): δ 130.5 (d, 2P, $^2J_{PP}$ = 54.9 Hz; [P(Me)Cl]), 100.6 (unresolved mult., 1P; [$C_6H_4N_2P(Me)$]) (**6A**); δ 124.9 (d, 2P, $^2J_{PP}$ = 26.7 Hz; [P(Me)Cl]), 107.7 (t, 1P; [$C_6H_4N_2P(Me)$]) (**6B**); δ 131.4 (d, 1P, $^2J_{PP}$ = 12.2 Hz; [P(Me)Cl]), 126.9 (d, 1P, $^2J_{PP}$ = 32.0 Hz; [P(Me)Cl]), 100.6 (unresolved multiplet, 1P; [$C_6H_4N_2P(Me)$]) (**6C**). ^1H (C_6D_6): δ 1.54 [d, 6H, J_{PH} = 13.1 Hz; P(CH_3)Cl], 0.68 [d, 3H, J_{PH} = 8.54 Hz; $C_6H_4N_2$(CH_3)] (**6A**); 1.64 (d, 6H, J_{PH} = 12.3 Hz; P(CH_3)Cl], 1.10 [d, 3H, J_{PH} = 8.33; $C_6H_4N_2$(CH_3)] (**6B**); 1.69 [d, 3H, J_{PH} = 12.3 Hz; P(CH_3)Cl], 1.52 [d, 3H, J_{PH} = 13.5 Hz; P(CH_3)Cl], 0.88 [d, 3H, J_{PH} = 8.54 Hz; $C_6H_4N_2$(CH_3)] (**6C**); 7.4−7.2 (complex multiplet, aryl H's), 6.8−6.7 (complex multiplet, aryl H's) (**6A**−**C**).

Alternatively, 1,2-$(NH_2)_2C_6H_4$ (0.54 g, 5.0 mmol) in acetonitrile (25 mL) was added dropwise to a solution of $MePCl_2$ (1.77 mL, 20.0 mmol) and Et_3N (3.5 mL) in acetonitrile (2 mL). After addition was complete, the [Et_3NH]Cl that formed was filtered off. Removal of volatile materials in vacuo yielded the **6A**−**C** oil in high purity (>90%).

$C_6H_4N_2[PhP(NH^iPr)]_2PPh$ (7A−C). A solution of $^iPrNH_2$ (2.36 mL, 34.6 mmol) in toluene (5 mL) was added, in portions, to **5A**−**C** (7.2 mmol) and Et_3N (4.82 mL, 34.6 mmol) in toluene (80 mL) at 25 °C. After 29 h, [Et_3NH]Cl was removed by filtration and the volume of solution was reduced in vacuo. This solution was subjected to flash column chromatography (ethyl acetate:petroleum ether = 4:1). Removal of solvents in vacuo yielded the viscous oil **7A**−**C** (mole ratio, 1.5:3.2:1.0). Anal. Calcd for $C_{30}H_{35}N_4P_3$: molecular mass, 544.2075 amu. Found: molecular mass (EI$^+$, accurate mass), 544.2067 amu. MS: EI$^+$, M$^+$, *m/z* 544 [$C_{30}H_{35}N_4P_3^+$]; CI$^+$, M + 1$^+$, *m/z* 545 [$C_{30}H_{36}N_4P_3^+$]. $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 98.1 (t, 1P, $^2J_{PP}$ = 137.4 Hz; PPh), 63.1 [d, 2P, $^2J_{PP}$ = 137.2 Hz; PhP(NH^{i}Pr)] (**7A**); δ 98.2 (t, 1P, $^2J_{PP}$ = 137.3 Hz; PhP), 62.6 [d, 2P, $^2J_{PP}$ = 137.8 Hz; PhP(NH^{i}Pr)] (**7B**); δ 97.0 (d of d, 1P, $^2J_{PP}$ = 163.5 Hz, $^2J_{PP}$ = 131.8 Hz; PhP), 62.7 [d of d, 1P, $^2J_{PP}$ = 163.5 Hz, $^2J_{PP}$ = 131.8 Hz; PhP(NH^{i}Pr)] (**7C**). ^1H NMR (C_6D_6, 20 °C): **7A**, δ 0.83 [d, $^3J_{HH}$ = 6.40 Hz; CH(CH_3)$_2$], 1.01 [d, $^3J_{HH}$ = 6.40 Hz; CH(CH_3)$_2$], 2.70 [d of d, *J* = 11.6 Hz, *J* = 7.9 Hz; NHCH(CH$_3$)$_2$], 6.98−7.04 [m; P(C_6H_5)NH(*i*-Pr)], 7.48−7.56 [m; C_6H_4(N)P(C_6H_5)]. Because of the complexity and overlapped nature of the remainder of the ^1H NMR spectrum, resonances corresponding to **7B** and **7C** could not be unambiguously assigned. Attempts to separate the diastereomers failed.

$C_2H_4N_2(PhPCl)_2PPh$ (8A−C) and $C_2H_4N_2[PhP(S)NEt_2]_2PPh$ (10A−C). $PhPCl_2$ (0.87 mL, 6.4 mmol) was added dropwise to a stirred solution of **4** (1.00 g, 1.54 mmol) in toluene (25 mL). After 8 h at 25 °C, ^{31}P NMR analysis showed complete formation of diastereomers **8A**−**C** (1.0:1.7:4.0 ratio). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 126.0 (d, 2P, $^2J_{PP}$ = 177 Hz), 104.2 (t, 1P) (**8A**); δ 127.6 (d, 2P, $^2J_{PP}$ = 243 Hz), 103.8 (t, 1P) (**8B**); δ 130.9 (d, 1P, $^2J_{PP}$ = 264 Hz), 124.6 (d, 1P, $^2J_{PP}$ = 203 Hz), 106.5 (d of d, 1P) (**8C**). Owing to the high reactivity of **8A**−**C**, further characterization was performed on aminated (thio) derivatives (below).

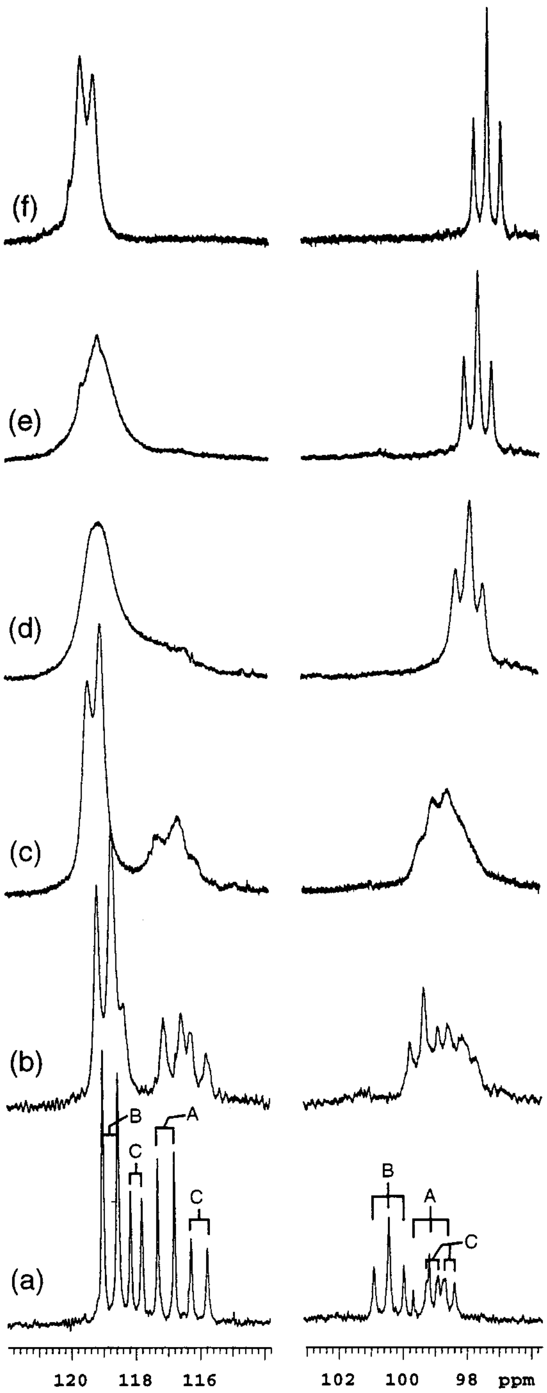


Figure 1. $^{31}P\{^1H\}$ NMR spectra (162.0 MHz) of **5A**−**C** at 22.0 °C in (a) neat toluene (ϵ = 2.43); toluene/acetonitrile mixures (b) 80.0 mol % toluene (ϵ = 5.46), (c) 60.0 mol % toluene (ϵ = 8.30), (d) 40.0 mol % toluene (ϵ = 15.0), (e) 20.0 mol % toluene (ϵ = 23.9); and (f) neat acetonitrile (ϵ = 37.4).

$^iPrNH_2$ (1.70 mL, 16.4 mmol) was added to the **8A**−**C** mixture. After 3 days the ^{31}P NMR spectral analysis showed conversion of **8A**−**C** to aminated products (**9A**−**C**). The [$^iPrNH_3$]Cl was filtered off, and S_8 (0.34 g, 11 mmol) was added. After 1 h, toluene was removed in vacuo. Recrystallization from CH_2Cl_2 yielded a crystalline isomer mixture **10A**−**C** (1.0:2.9:4.2 ratio). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 72.8 (t, 1P, $^2J_{PP}$ = 12 Hz), 69.6 (d, 2P) (**10A**); δ 74.0 (t, 1P, $^2J_{PP}$ = 6.0 Hz), 71.7 (d, 2P) (**10B**); δ 73.3 (d of d, 1P, $^2J_{PP}$ = 13.2, $^2J_{PP}$ = 5.5 Hz), 72.1 (d of d, 1P, $^2J_{PP}$ = 5.5, $^2J_{PP}$ = 2.8 Hz), 69.3 (d of d, 1P, $^2J_{PP}$ = 13.2, $^2J_{PP}$ = 2.8 Hz) (**10C**). MS: EI, M$^+$, *m/z* 620 [$C_{28}H_{39}P_3N_4S_3^+$].

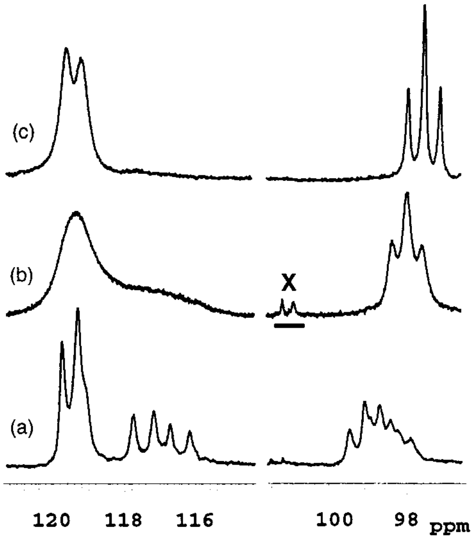
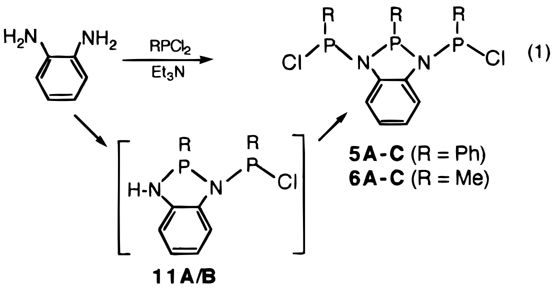


Figure 2. ^{31}P{^{1}H} NMR spectra (162.0 MHz) of **5A−C** at 22.0 °C in (a) CH_2Cl_2 ($\epsilon = 9.1$), (b) nitrobenzene ($\epsilon = 34.8$), and (c) pyridine ($\epsilon = 12.3$). The X in spectrum b designates small impurity peaks.

Anal. Calcd for $C_{28}H_{39}P_3N_4S_3$: C, 54.19; H, 6.30; N, 9.03; molecular mass, 620.1550 amu. Found: C, 54.82; H, 6.39; N, 9.22; molecular mass (EI^{+}, accurate mass, MS), 620.1550 amu.

NMR Studies. ^{31}P{^{1}H} NMR spectra of **5A**,**B** and **6A−C** as a function of temperature were obtained on the VXR 300S and Inova-500 in (temperature range): *m*-xylene (−50 to 130 °C) (Figure 3), CH_2Cl_2 (−78 to 30.0 °C), and MeCN (−30.0 to 30.0 °C). Spectra of **5A−C** at 22 °C were obtained: as a function of dielectric constant (ϵ) in pure xylene ($\epsilon = 2.43$)[10] and MeCN ($\epsilon = 37.4$)[10] and in toluene/MeCN solutions over the dielectric constant range of $\epsilon = 5.46$ to $\epsilon = 23.9$ (Figure 1a−f); in nitrobenzene ($\epsilon = 34.8$,[10] Figure 2b); in pyridine ($\epsilon = 12.3$,[10] Figure 2c); in CH_2Cl_2 ($\epsilon = 9.1$,[10] Figure 2a); in CH_2Cl_2 saturated with $AlCl_3$; and in CH_2Cl_2 saturated with $[Me_4N]Cl$.

Results and Discussion



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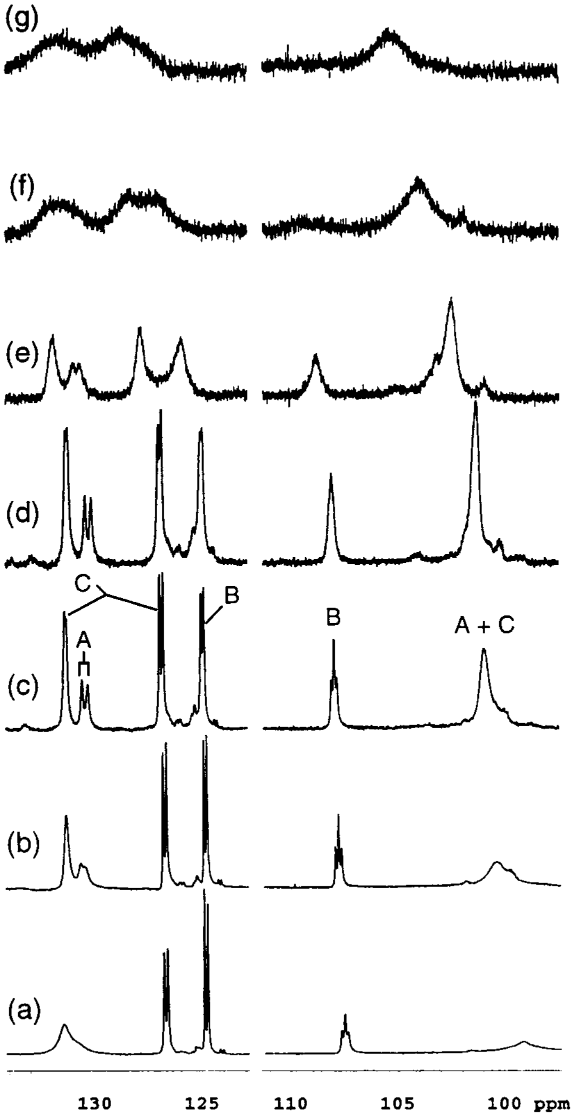
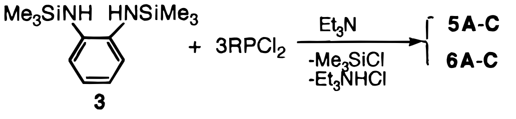


Figure 3. ^{31}P{^{1}H} NMR spectra (202.6 Mz) of **6A−C** in *m*-xylene at (a) −50 °C, (b) −30 °C, (c) −10 °C, (d) 10 °C, (e) 50 °C, (f) 90 °C, and (g) 130 °C.

Three new dichlorotriphosphazanes, **5A−C**, **6A−C**, and **8A−C**, as mixtures of diastereomers were prepared in this study. Reactions of $1,2\text{-}(NH_2)_2C_6H_4$ with 3 equiv or more of $RPCl_2$ (R = Me, Ph) in the presence of Et_3N to scavenge HCl proceed efficiently to **5A−C** and **6A−C** (eq 1). Reactions occur smoothly at 25 °C in either toluene or acetonitrile, forming first the tentatively characterized diphosphazane diastereomers **11A/B**[3] which appear fleetingly as two equal-area pairs of doublets in the ^{31}P NMR spectra of the reaction solutions. Products are typically isolated by removing first the $[Et_3NH]Cl$ by filtration and then the volatile reaction materials in vacuo. Triphosphazanes **5** and **6** are formed in high yield using 3:1 or greater $RPCl_2$:$1,2\text{-}(NH_2)_2C_6H_4$ reactant ratios. Under similar conditions, $PhPCl_2$ and ethylenediamine react readily to form **8A−C**; however, since they are minor products in a complex mixture of other unidentified materials, this reaction was not pursued. Compounds **5A−C** and **6A−C** also can be prepared optimally from reactions of excess $PhPCl_2$ or $MePCl_2$ with $1,2\text{-}(Me_3SiNH)_2C_6H_4$ (**3**) in the presence of Et_3N according to eq 2.



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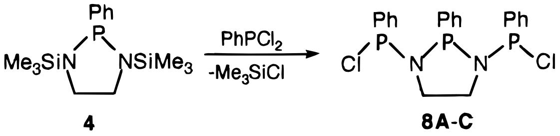

(3)

However, because the silylamine **3** is not easily available, the $1,2\text{-}(NH_2)_2C_6H_4$/$RPCl_2$ (R = Me, Ph) reactions are preferred for general synthetic applications. Reaction of 2 equiv of $PhPCl_2$ with the bis(silyl)phosphadiazole **4** for 10 h yields the dichlorotriphosphazanes **8A−C**. The latter are cleanly formed; removal of solvent results in their decomposition to higher molecular weight, uncharacterizable materials.

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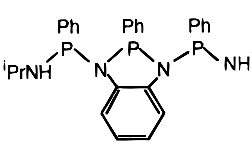
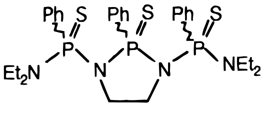
(10) *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1989.

Characterization of **5A−C** and **6A−C** is based on spectral data. For **5A−C** and **8A−C**, additional characterization is obtained from examination of their amination or amination/thio derivatives, respectively. Reaction of **5A−C** with ^{i}PrNH$_2$ or **8A−C** with Et$_2$NH and elemental sulfur yielded **7A−C** and **10A−C**. Compound **7A−C**, like the dichlorotriphosphazanes, did not crystallize. The amino/thio λ^4 sulfide diastereomers **10A−C** crystallized, but without any isomer separation. The three new dichlorotriphosphazanes **5A−C**, **6A−C**, and **8A−C** and the derivatives **7A−C** and **10A−C** exhibit mass spectral molecular ions; their elemental compositions are confirmed by exact mass spectral analysis.

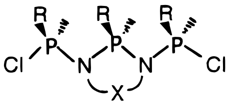


7A-C

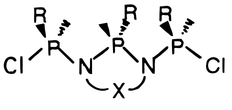


10A-C

The ^{31}P NMR spectra of the dichlorotriphosphazanes **5A−C** (Figure 1a), **6A−C** (Figure 3c), and **8A−C** and the derivatives **7A−C** and **10A−C** in nonpolar solvents show them to be mixtures of three diastereomers. For **5A−C**, **6A−C**, and **7A−C** the *meso*:*meso′*:*d,l* ratios are all within the range 1.0:1.4−1.8: 1.3−4.0. In each case these are taken to be thermodynamic mixtures, and they do not vary significantly from the statistically expected ratios of *meso*:*meso′*:*d,l* = 1:1:2. In all of these cases one *meso* isomer is slightly favored, and in the **6A−C** and **8A−C** mixtures the *d,l* is slightly favored. For **5A−C**, **6A−C**, and **8A−C**, resonances due to the *exo* −P(R)Cl groups all occur in the range δ 116.2−132.2, in the region expected.[11] Similarly, the *endo* λ^3 P centers occur at higher field in the typical range[11,12] of δ 98.8−106.5. The spectra of **5A−C** and **8A−C** and the amino/thio derivative of **8A−C**, **10A−C**, show two well-resolved doublet (2P) and triplet (1P) AX$_2$[13] patterns attributable to the two *meso* forms, **A** and **B**. Each spectrum exhibits a three-resonance AMX[13] pattern of single phosphorus resonances due to the *d,l* isomer (**C**). For **5C** and **8C**, the patterns appear as two 2P doublets and a 1P doublet of doublets (d of d) resonances from existence of two $^{2}J_{PP}$ coupling constants, whereas in the λ^4 derivative **10C**, all three resonances appear as doublets of doublets. For **6A−C** and **7A−C**, even though the high-field *endo* P resonances are of correct relative area, at 25 °C the resolution of the peaks was not adequate to allow identification of each multiplet type.

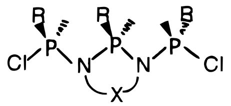


5,6,8 (A or B)
(*meso*)



5,6,8 (B or A)
(*meso′*)

5: R = Ph, X = C$_6$H$_4$
6: R = Me, X = C$_6$H$_4$
8; R = Ph, X = C$_2$H$_4$



5,6,8C
(*d,l*)

The ^{31}P NMR spectra of the dichlorotriphosphazanes are dependent on both solvent and temperature, and from an examination of the spectra as a function of (i) solvent donor strength, (ii) solvent polarity (dielectric constant), and (iii) temperature, we have obtained information about the dynamic properties of these species.

Solvent Polarity/Donor Effects. The spectra of **5A−C**, **6A−C**, and **8A−C** in weakly coordinating, low dielectric constant solvents such as toluene (ϵ = 2.43)[10] exhibit three distinct resonance patterns attributable to the three (*meso*, *meso′*, and *d,l*) diastereomers, e.g., that of **5A−C** obtained at 121.4 MHz is shown in Figure 1a. The diastereomer ratio is 1:1.4:1.3. It is assumed that all three diastereomers are conformationally nonrigid, a reasonable assumption since the barriers to rotation around phosphazane P−N bonds is generally in the range 33−56 kJ/mol.[14] In contrast, in the polar coordinating solvent acetonitrile (ϵ = 37.4) the spectrum appears as an AX$_2$ area 2 doublet and area 1 triplet, averaged spectrum (e.g., Figure 1f). The transition from a spectrum of three distinct diastereomers, through degrees of spectral collapse, to the final average spectrum is shown in the toluene/acetonitrile solution series in Figure 1a−f. The spectral effect is reversible; if the acetonitrile is removed in vacuo and replaced by toluene, the spectrum is superimposable with the original spectrum in toluene.

The collapse from a three-diastereomer spectrum to a single average AX$_2$ pattern is not primarily a solvent dielectric effect. This is shown by examination of the spectra of **5A−C** at 25 °C in CH$_2$Cl$_2$ (Figure 2a), nitrobenzene (Figure 2b), and pyridine (Figure 2c). On the basis of known base donor data,[15,16] these are expected to increase in donor strength toward a P(III) center as CH$_2$Cl$_2$ < C$_6$H$_5$NO$_2$ < pyridine. In the CH$_2$Cl$_2$, a weakly coordinating, intermediate dielectric solvent (ϵ = 9.08), the spectrum is only slightly collapsed. In nitrobenzene, which is a high-dielectric medium (ϵ = 34.8) but only a moderate donor, the spectrum is only partially collapsed and about equal to that of the toluene/MeCN solution at dielectric strength ϵ = 15.0 (Figure 1d). Finally consistent with this pattern, in pyridine, which is a strong donor but an intermediate dielectric solvent (ϵ = 12.3), the spectrum is completely collapsed to the AX$_2$ pattern (Figure 2c).

The effect of solvent polarity on spectral appearance suggests the occurrence of a dynamic process in which the *endo* and *exo* phosphorus environments of the three diastereomers become, on the time scale of the NMR experiment, as one *exo* and one *endo* environment. Two processes to be considered that could account for this averaging are illustrated in Scheme 1 for one isomer (*trans,trans-meso* isomer) of the **5A−C** mixture, one mechanism involving dissociation to a phosphenium ion (**12a**)[17] and another involving a five-coordinate intermediate (**12b**). Either exchange process must involve structural rearrangement for the three diastereomer spectra to collapse to an average

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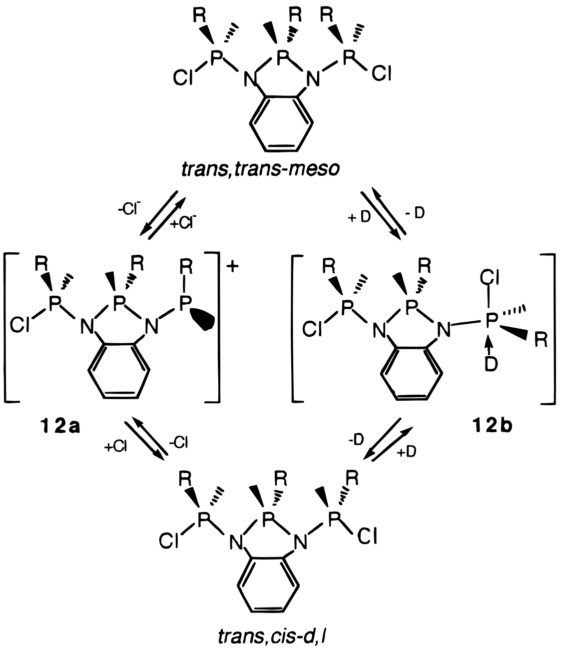
Scheme 1



spectrum. If dissociation of either of the two *exo* −P(R)Cl P−Cl bonds of the chlorophosphazane occurs to form **12a**, in which the P center becomes trigonal planar, it is necessary that it be equally likely that the R group of **12a** rearrange to either the *trans,trans* or *trans,cis* isomeric arrangement. Likewise, through pseudorotation,[18] the five-coordinate **12b** could rearrange to either isomer prior to dissociation of the donor molecule. Since we know that diastereomers **5A−C** are approximately equally stable, there would be no great preference for the Ph group of either intermediate to go back to the *trans,trans* arrangement over going to the *trans,cis* arrangement. This tendency would lead to averaging at the *exo* center. This effect happening at both *exo* groups of each diastereomer would result in the *exo* and *endo* P environments each becoming of one type in which the *endo* P sees both trans- and *cis*-located Ph groups equally and the *exo* groups see both *cis* and *trans* configurations equally.

Whereas higher donor strength solvents should favor **12b**, they could also facilitate dissociation to the phosphenium ion intermediate by weak coordination at the phosphorus center. Furthermore, both processes could be favored by higher dielectric constant solvents, since in the phosphenium ion case and perhaps in the five-coordinated case, intermediate polarity would be higher than reactant polarity, and equilibrium to the intermediates should be favored. However, when $AlCl_3$ is added to CH_2Cl_2 solutions of **5A−C**, which should promote phosphenium ion formation[17,19] and enhanced exchange, no significant spectral collapse occurs. The dichlorotriphosphazanes apparently are not prone to loss of a chloride ion. Furthermore, when $[Me_4N]Cl$ is added to a solution of **5A−C** in CH_2Cl_2, no effect is seen, in contrast to that expected if there is equilibrium involving intermediate **12a**. Thus, on the basis of our data we conclude that the major process by which diastereomer averaging occurs involves a five-coordinate intermediate (**12b**), and it is its formation upon coordination of strong donors such as pyridine that causes spectral averaging.

Temperature Effects. The ^{31}P NMR spectra of the dichlorotriphosphazanes are temperature dependent, yielding important conformational information. Spectral effects in solvents of low dielectric constant, e.g., toluene or xylene, are especially interesting because, in these, isomer averaging is minimal. For example, the spectra of **6A−C** in *m*-xylene between −50 and 130 °C at 202.6 MHz are shown in Figure 3; the data show that the three diastereomers are not affected equally. The spectrum is most readily interpreted at −10 °C. Both below and above −10 °C, spectral broadening is seen. At −10 °C (Figure 3c), the spectrum shows two 2P doublet resonances in the low-field −P(Cl)Ph region at δ 130.5 and 124.9 due to *meso* isomers **6A** and **6B** and two equal-area 1P doublets at δ 131.4 and 126.9 due to the *d,l* isomer **6C**. In the *endo* $N_2P(Ph)$ region the expected triplet resonance from **6B** is seen. The *endo* phosphorus resonances from to **6A** and **6C** are overlapped and not resolvable. Coupling constants can be measured reliably only in the low-field (*exo*) region for **6A** and **6C**; however, for **6B**, the $^2J_{PP}$ value can be measured in both the *exo* and *endo* phosphorus resonances. The $^2J_{PP}$ values for **6A** and **6B** at −10 °C are 54.9 and 26.7 Hz, respectively, and the two $^2J_{PP}$ values for **6C** are 12.2 and 32.0 Hz. As the sample is cooled to −30 °C and then to −50 °C, spectral broadening and a decrease of $^2J_{PP}$ values occurs for the overlapped *endo* P resonances of **6A** and **6C**, the *exo* resonance of **6A**, and the lowest field *exo* resonance of **6C**. In contrast, the **6B** resonances and one **6C** *exo* resonance at δ 126.9 remain resolved and for each of these the $^2J_{PP}$ values increase to 32.0 and 34.3 Hz, respectively. When warmed above −10 °C, all resonances begin to collapse, apparently to one spectral pattern that is the average of all three diastereomers (e.g., Figure 3g). One can speculate that above 130 °C a single 2P triplet and 1P doublet spectrum might be achieved, not unlike what is seen in the high-polarity solvents.

At least two processes must be considered in order to explain the temperature effects in **6A-C**. Above −10 °C all three diastereomers are taken to be essentially conformationally nonrigid. Each diastereomer's spectrum is the average of the conformational states accessed. As the temperature is lowered, effects are seen that result from conformation rotational changes. Resonance collapse occurs because of the onset of −P(Cl)Me group restricted rotation around the *exo* P−N bonds.[14] Resonances whose $^2J_{PP}$ values increase and which do not broaden [at δ 124.9 and 107.7 (**6B**) and 126.9 (one *exo* of **6C**)] could result from a shift in the conformational population toward a state of higher $^2J_{PP}$.[20] At some lower temperature, we might expect each diastereomer's spectrum to coalesce and reemerge as the spectrum of one preferred conformational state.

The spectra suggest that there are small differences in the barriers to rotation of the *exo* −P(Cl)Me groups in the three diastereomers. One *meso* isomer (**6A**) shows symmetrically restricted rotation, and the other (**6B**) shows no significant restriction even at −50 °C. Moreover, the *d,l* isomer (**6C**) shows greater rotational restriction of one *exo* site than the other. This can be explained by recognizing that in the *d,l* isomer there are *exo* groups of the type shown in each of the *meso* isomers, a situation shown graphically:

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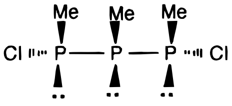
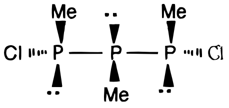
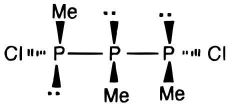


6A (*cis,cis-meso*)



6B (*trans,trans-meso*)



6C (*trans,cis-d,l*)

In one *meso* isomer the Me groups are in a *trans* relationship to the central Me group, whereas in the other they are in a *cis* relationship. However, in the *d,l* isomer, one Me group is *cis* and the other *trans* to the central Me. On the basis of examination of models, we suggest that (i) the rotation will be more restricted for the *cis-exo* Me than the *trans-exo* Me, and therefore (ii) the isomers **6B** and **6A** are the *trans,trans* and *cis,cis* arrangements, respectively. Furthermore, in **6C** the *trans-exo* groups will be the least restricted and it is its resonance, i.e., that at δ 126.9 that does not broaden upon cooling to −50 °C. Because of the spectral complexity, no attempt was made to determine the relative rotational barriers in the three diastereomers.

The effect that a polar solvent has on the average dichlorotriphosphazane diastereomer composition might have important implications as to what to expect in subsequent reactions. For example, in ring closure reactions it might be expected that, of the three diastereomers, only one will have the correct stereochemistry to participate, whereas the other diastereomers will react to form acyclic oligomers or polymers. However, in a polar solvent like acetonitrile, if the ring closure reaction is faster that linear chain extension, all isomers might ultimately participate in the ring closure process. Studies of such reactions are underway and will be reported later.

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