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Reactions of *N*-Silylphosphoranimines with Alcohols: Synthesis and Structure of Cyclotriphosphazenes with Nongeminal Methyl and Phenyl Substituents

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The reactions of $Me_3SiN{=}P(OR'')RR'$ ($R'' = Ph$, CH_2CF_3; R, $R' = Me$, Ph) with alcohols were investigated. With nonequivalent amounts of CF_3CH_2OH, the reactions produced high yields of the cyclic phosphazene $(Me_2PN)_3$ and both the *cis* and *trans* isomers of *nongeminally* substituted $[(Ph)(Me)PN]_3$. The isomers of this new cyclic phosphazene were separated by column chromatography and characterized by NMR and IR spectroscopy, elemental analysis, and X-ray crystallography. Crystals of the *cis* isomer **6a** have a monoclinic crystal system, while the *trans* isomer **6b** has a triclinic crystal system with two different molecules in an asymmetric unit. The bond lengths and bond angles are very similar to those of the simpler cyclic trimers $(Me_2PN)_3$ and $(Ph_2PN)_3$. A likely pathway for the formation of these compounds is discussed.

Introduction

Cyclic phosphazenes with alkyl or aryl groups attached to the phosphorus atom have been prepared by several methods. For example, the cyclic methylphosphazenes $(Me_2PN)_{3-7}$ can be obtained from the reaction of dimethyltrichlorophosphorane with chloramines or amines[1,2] or by the alkylation of cyclic fluorophosphazenes.[3] A related trimeric phosphazene, $[Ph_4Me_2P_3N_3]$, with geminally substituted methyl and phenyl groups was synthesized from the reaction of Me_2PCl_3 and bis(aminodiphenylphosphine)-iminium chloride.[4] The nongeminally substituted alkyl and aryl analogues $[alkyl(aryl)PN]_3$, however, are not readily accessible by these approaches due to the challenging syntheses of the precursor phosphoranes[5] and to the predominance of the geminal substitution pathway in cyclic halophosphazenes.[6] The cyclic phosphazene $[Me(Ph)P{=}N]_3$ is of particular interest because the formation of two isomers of this compound offers unique opportunities for stereochemical and structural control. Moreover, its polymeric analogue $[Me(Ph)P{=}N]_n$[7,8] has been well studied and exhibits interesting reactivity patterns[9] that could provide access to a variety of structurally diverse cyclic analogues with unusual shape and reactivity. We report here the preparation, isolation, and characterization of both the *cis* and the *trans* isomers of the unusual nongeminally substituted cyclic phosphazene trimer $[Me(Ph)PN]_3$.

Results and Discussion

N-Silylphosphoranimines of general formula $Me_3SiN{=}P(X)R'R''$ have provided access to a variety of new main group element systems, especially phosphazene polymers. Studies in our laboratories have shown that these Si−N−P

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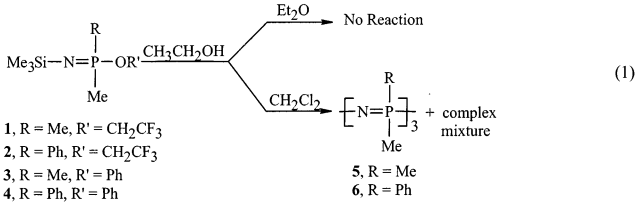
compounds exhibit at least four modes of reactivity: (1) condensation to polymeric[7] ($X = OCH_2CF_3$ or OPh) or cyclic and/or oligomeric[10] (X = halogen) phosphazenes via elimination of Me_3SiX, (2) substitution at phosphorus,[11] (3) deprotonation−substitution at *P*-alkyl groups,[12] and (4) Si−N bond cleavage reactions.[13] The utility of *N*-silylphosphoranimines is enhanced by their straightforward and versatile synthesis.[8] As part of our ongoing studies of this class of compounds, an investigation was initiated to prepare and isolate the nonsilylated H−N analogues H−N=P(X)R′R. In the course of this work, we found that the *N*-silylphosphoranimines are readily and cleanly converted to nongeminal methylaryl-substituted cyclic phosphazenes in reasonably fast reactions at room temperature.

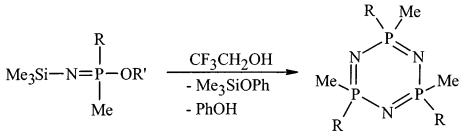
While *N*-silyl-*P*-*trialkyl*phosphoranimines can be converted to the N−H analogues by treatment with methanol in the presence of trace amounts of acid,[14] complex mixtures were obtained under similar conditions when the substituents at phosphorus were more reactive non-alkyl groups such as CF_3CH_2O groups.[15,16] Since these mixtures probably resulted from hydrolysis reactions caused by trace amounts of H_2O, the reactions of phosphoranimines with anhydrous alcohols were investigated. The reactions of four different phosphoranimines with ethanol were solvent dependent (eq 1). In



(1)

diethyl ether, no reaction occurred after 5 h, but in dichloromethane, complicated mixtures or decomposition products resulted, as demonstrated by multiple signals in the ^{31}P NMR spectra. Recrystallization of the white solid residues produced low yields of cyclic compound **5** or **6**, which was identified by ^{31}P NMR spectroscopy and GC/mass spectrometry.

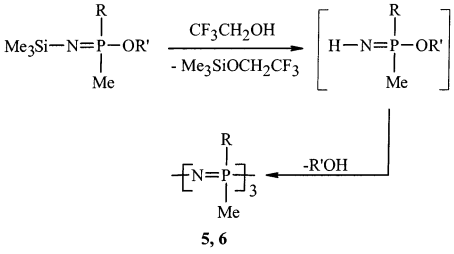
Since no N−H phosphoranimines were obtained from ethanol, the reactions of the more acidic reagent trifluoroethanol were investigated.[17] Once again, no evidence for the formation of N−H phosphoranimines was observed; however, under anhydrous conditions, the reaction with either the *P*-phenoxy- or *P*-trifluoroethoxy-*N*-silylphosphoranimines proceeded at room temperature to give good yields of cyclic phosphazenes (eq 2), including the previously inaccessible



(2)

nongeminally substituted $[Me(Ph)PN]_3$, **6**. The ^{31}P NMR spectra of the reaction mixtures and crude products after removal of volatiles clearly showed that only the cyclic trimers, and no tetramers or larger ring compounds, had formed.

Although the formation of N−H phosphoranimines was not observed, it is likely that they are intermediates formed by protonation of nitrogen with loss of $Me_3SiOCH_2CF_3$ and subsequent elimination of the alcohol R′OH (eq 3). This is



(3)

substantiated by the difficulty in purification of the cyclic compounds **5** and **6** as discussed below. In particular, large amounts of PhOH were formed in these reactions where R′ was a phenyl group.

The known compound **5** was isolated by recrystallization from CH_2Cl_2–hexane. It was identified by NMR spectroscopy (^{31}P, δ 27.0) and the melting point (195 °C).[18] Purification of **6**, however, was less straightforward since both the *cis* and the *trans* isomers are formed (^{31}P, δ 19.6, 20.3, 20.4; see the discussion below). In general, the trifluoroethoxyphosphoranimines **1** and **2** did not react as cleanly as the phenoxy analogues **3** and **4**. While a 5% mol equiv of CF_3CH_3OH resulted in complete reaction for the phenoxy compounds, even 10% mol equiv did not give complete reaction of the trifluoroethoxyphosphoranimines.

Although the reactions were investigated with and without adding solvents such as Et_2O or CH_2Cl_2, the best results were obtained from the reactions of the phosphoranimines with CF_3CH_2OH in the absence of solvent. This gave cleaner, faster reactions and afforded high, synthetically useful yields of the cyclic phosphazenes. Moreover, the isolation of clean samples of the cyclic compounds was facilitated by washing dichloromethane solutions of the cyclics with aqueous KOH to remove PhOH, which is strongly hydrogen-bonded to the lone pair on the nitrogen atoms in the ring. The basicity of this nitrogen, which is enhanced by the electron-releasing alkyl and aryl groups, has been investigated for related cyclic

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(17) It should be noted that treatment of the *N*-silylphosphoranimines with an even more acidic reagent, i.e., benzoic acid, failed to yield cyclic phosphazenes. The crude products formed in these reactions appear to be unstable *N*-phosphorylphosphoranimines on the basis of NMR spectroscopic data.
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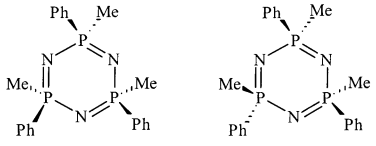
phosphazenes[4] and for the polymer analogues.[19] Gram quantities of both the *cis* and *trans* isomers of **6**, $[(Me)(Ph)PN]_3$, were obtained using column chromatography. In the early reactions carried out in the presence of diethyl ether, small amounts of the *cis* isomer were isolated by slow recrystallization from CH_2Cl_2, but this did not allow for separation of the large amounts of the isomers that remained in solution.

The isomers of the new cyclic compound **6** were characterized by elemental analysis, melting points, IR and NMR spectroscopy, and X-ray diffraction studies. Strong IR absorbances between 1100 and 1300 cm^{-1} are indicative of the phosphorus−nitrogen bond in the ring.[20] As expected the melting point of the more symmetrical *cis* isomer **6a** is higher (157 °C) than that of the *trans* isomer **6b** (97 °C).



The ^{31}P NMR spectra were relatively simple with a single signal for the *cis* isomer (δ 19.6) and two signals in a roughly 2:1 ratio for the *trans* isomer (δ 20.3, 20.4). No long-range phosphorus−phosphorus coupling was observed. The ^1H NMR spectra showed the expected methyl and phenyl signals for both isomers, and for the *cis* isomer, coupling to both the nearest and the more distant phosphorus atoms was observed, i.e., $^2J_{PH} = 14.2$ Hz and $^4J_{PH} = 1.7$ Hz. The ^{13}C NMR spectra clearly showed both the short and long-range coupling to phosphorus for the methyl carbons (i.e., doublets of triplets) and coupling between the carbon atoms of the phenyl group and the nearest phosphorus nucleus. The P═N stretching frequencies in the IR spectra were observed at 1186 and 1170 cm^{-1} and 1183 and 1167 cm^{-1} for the *cis* and *trans* isomers, respectively. These are almost identical to the values reported for $(Me_2PN)_3$ and $(Ph_2PN)_3$[20] and are consistent with the electron-releasing effects of the methyl and phenyl substituents.

The X-ray crystal structures of **6a** (Figure 1) and **6b** (Figure 2) were determined. The crystal data are presented in Table 1, and selected bond distances and angles are given in Table 2. The bond lengths and bond angles in both the new nongeminal isomers **6a** and **6b** are similar to those of the closely related cyclic trimers $(Me_2PN)_3$[21] and $(Ph_2PN)_3$.[22] Isomer **6a** crystallizes in the monoclinic crystal system, and the molecule has a *cis* configuration (Figure 1) with all three phenyl groups on the same side of the almost planar six-membered P_3N_3 ring. Isomer **6b** has a triclinic crystal system and a *trans* stereochemistry (Figure 2) with two phenyl groups on one side of the nearly planar P_3N_3 ring and one phenyl group on the opposite side of the ring. There are two different molecules of **6b** in an asymmetric unit, but their basic geometry is the same.

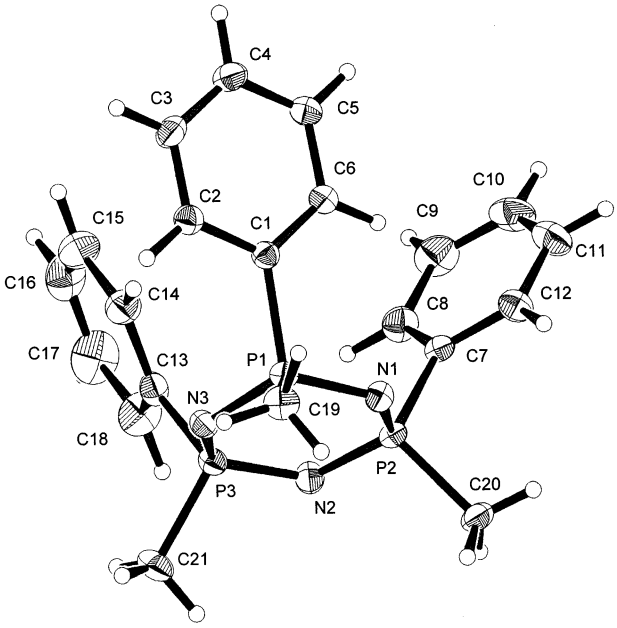


Figure 1. Thermal ellipsoid plot of **6a**, *cis*-$(Me(Ph)P{=}N)_3$ (40% probability ellipsoids for non-hydrogen atoms are shown).

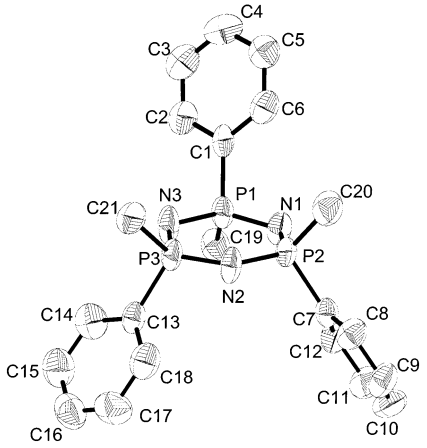


Figure 2. Thermal ellipsoid plot of **6b**, *trans*-$(Me(Ph)P{=}N)_3$ (40% probability ellipsoids for non-hydrogen atoms are shown).

The four atoms P(1), P(3), N(1), and N(2) in **6a** are essentially coplanar. The other two atoms of the cyclic phosphazene ring, P(2) and N(3), deviate slightly from the plane by +0.292 and −0.233 Å for P(2) and N(3), respectively. Similarly, P(2), P(3), N(1), and N(2), as well as P(5), P(6), N(4), and N(5), are coplanar in the two independent molecules of **6b**. The out-of-plane atoms are located on the same side of the relevant phosphazene plane, P(1) −0.112 Å, N(3) −0.158 Å, and P(4) −0.150 Å, N(6) −0.236 Å, respectively. By these deformations, the P_3N_3 rings of **6a** and **6b** have a slightly chair and puckered form, respectively, due to intra- and intermolecular steric effects as observed for $(R_2PN)_3$ (R = Me or Ph) and to slight steric repulsions of the phenyl groups.[21,22] As shown in Table 2, all the P−N bond lengths are approximately 1.60 Å (1.595−1.603 Å) in

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Table 1. Crystallographic Data for Cyclic Phosphazene Isomers **6a** and **6b**

	6a	**6b**
empirical formula	$C_{21}H_{24}O_3P_3$	$C_{21}H_{24}O_3P_3$
fw	411.36	411.36
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	10.713(1)	8.128(2)
b, Å	21.127(2)	15.809(3)
c, Å	10.869(2)	17.454(3)
α, deg	90	107.93(1)
β, deg	118.300(9)	90.59(2)
γ, deg	90	91.58(1)
V, Å^3	2166(1)	2132.6(8)
Z	4	4
λ, Å	1.54178	0.71073
ρ_{cald}, g cm^{-1}	1.261	1.281
μ, mm^{-1}	2.623	0.290
R1 [$I > 2\sigma(I)$][a]	0.038	0.095
wR2 [all data]	0.041[b]	0.236[c]

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

6a and 1.60 Å (1.575−1.618 Å) in **6b**, while all P−N−P bond angles are about 121° (121.0−121.8°) in **6a** and 123° (120.9−124.7°) in **6b**. The N−P−N angles are ca. 117° (116.8−117.1°) in **6a** and 117° (115.9−118.0°) in **6b**, and the exocyclic R−P−R bond angles are about 104° (103.6−104.4°) in **6a** and about 103° (102.1−105.4°) in **6b**. The *P*-aryl distances for **6a** [mean 1.811(3) Å] and **6b** [mean 1.807(8) Å] are close to the typical *P*-aryl distance of $(Ph_2P{=}N)_3$ [av 1.804 Å].[22] The *P*-alkyl distances for **6a** [mean 1.791(2) Å] and **6b** [mean 1.785(15) Å] are slightly shorter than in the analogous $(Me_2P{=}N)_3$ [av 1.805(4) Å].[21]

Thus, like their polymeric analogues, P−C-substituted cyclic phosphazenes can be prepared from *P*-aryloxy-*N*-trimethylsilylphosphoranimines. The trimer $(Me_2PN)_3$ and both the *cis* and *trans* isomers of *nongeminally* substituted $[(Me)(Ph)PN]_3$ are readily accessible by this approach. It is likely that these compounds result from initial formation and subsequent decomposition of elusive N−H phosphoranimines. While we have previously observed some formation of cyclic phosphazenes from *P*-halo-*N*-trimethylsilylphosphoranimines, these reactions required heating and gave more complex mixtures including cyclics with varying ring sizes and oligomers, presumably because of difficulty in purification of the *P*-halo compounds. Hence, the room-temperature reactions of *P*-aryloxyphosphoranimines described here provide a facile synthesis of P−C-substituted cyclic phosphazene trimers. The derivative chemistry of both the *trans* and the basket-like *cis* isomers of $[(Me)(Ph)PN]_3$ and the preparation of other nongeminal cyclic phosphazenes are under investigation in our laboratories.

Experimental Section

Materials and General Procedures. The *N*-silylphosphoranimines $Me_3SiN{=}P(OR')(Me)R$ [R′ = Ph, CH_2CF_3; R = Ph, Me], **1**−**4**, were prepared by published procedures.[8,10] 2,2,2-Trifluoroethanol was freshly distilled from barium oxide before use. Dichloromethane, diethyl ether, benzene, and hexane were distilled from CaH_2, while ethyl acetate was used as received from commercial sources. All manipulations for the synthesis of the *N*-silylphosphoranimine precursors were done under an atmosphere of dry nitrogen. The cyclic phosphazene products were handled in the air.

Equipment. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on an SGI/Bruker DRX-400 spectrometer or a Varian XL-300 spectrometer using $CDCl_3$ or DMSO-d_6 as a solvent. Positive ^1H and ^{13}C NMR chemical shifts and ^{31}P NMR shifts are downfield from the external references Me_4Si and H_3PO_4, respectively. Elemental analyses were obtained on a Carlo Erba Strumentazione CHN elemental analyzer 1106 or were done by the E+R Microanalytical Laboratory, Inc., Corona, NY. Melting points were determined on a TA Instruments DSC 2010 calorimeter. GC/mass spectrometry was done using a Hewlett-Packard 5890 gas chromatograph and 5989A mass spectrometer system.

X-ray Crystallography. Both isomeric phosphazenes are colorless. Diffraction data of **6a** were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα radiation, λ = 1.54178 Å, while those of **6b** were obtained on a Bruker P4 diffractometer with Mo Kα radiation, λ = 0.71073 Å. Both data sets were collected at room temperature. Crystallographic data are summarized in Table 1. Structure **6a** was solved using direct methods[23] and refined using the Texsan program package.[24] Structure **6b** was also solved using direct methods and subsequent Fourier synthesis with SHELXTL[25] with refinement by full-matrix least-squares methods against F^2 (SHELX97).[26] There are two independent molecules in an asymmetric unit in the lattice of **6b**. All non-hydrogen atoms were refined anisotropically, and the H atoms were constrained with a riding model. Selected bond distances and angles are listed in Table 2. Further details regarding the crystal data and refinement, as well as full tables of bond lengths and angles for each structure reported in this paper, are presented in CIF format in the Supporting Information.

Reactions of *N*-Silylphosphoranimines 1−4 with Ethanol. A 50 mL, three-neck, round-bottom flask, equipped with a magnetic stirring bar, a nitrogen inlet adapter, and a glass stopper, was charged with CH_2Cl_2 (20 mL) and *N*-silylphosphoranimine **1**, $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (5.0 g, 20.0 mmol). Then C_2H_5OH (1.2 mL, 20.0 mmol) was added dropwise via a syringe while the solution was stirred. After the solution was stirred for 1 h at room temperature, all volatile materials were removed under reduced pressure while some white solid was left in the flask. The white solid was then dissolved in CH_2Cl_2 and crystallized from a CH_2Cl_2–hexane solution to give colorless crystals of compound **5** (yield ∼35%). For the other phosphoranimines, the results were less clear-cut, giving low yields of **5** or mixtures of isomers of **6** as identified by ^{31}P NMR spectroscopy and GC/mass spectrometry.

Synthesis of $[Me_2)PN]_3$, 5. A 50 mL, three-neck, round-bottom flask, equipped with a magnetic stirring bar, a nitrogen inlet adapter, and a glass stopper, was charged with ether (20 mL) and *N*-silylphosphoranimine **1**, $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (5.0 g, 20.0 mmol). Then $HOCH_2CF_3$ (1.5 mL, 20.0 mmol) was added dropwise via a syringe while the solution was stirred. The reaction mixture was stirred at room temperature overnight, during which time white solids formed. Volatile materials were removed under reduced pressure, and a white solid residue was left. The white solids were

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(24) *Texsan-Texray Structure Analysis Package*, version 1.701; Molecular Structure Corp., March 1995.
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(26) Sheldrick, G. M. *SHELX97, Program for Crystal Structure Solution and Refinement*; Institute fur Anorganische Chemie: Göttingen, Germany, 1998.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6a**, *cis*-(Me(Ph)P═N)$_3$, and **6b**, *trans*-(Me(Ph)P═N)$_3$

6a					
P(1)−N(1)	1.601(2)	P(3)−N(2)	1.595(2)	P(2)−C(7)	1.808(2)
P(1)−N(3)	1.602(2)	P(3)−N(3)	1.601(2)	P(2)−C(20)	1.791(3)
P(2)−N(1)	1.596(2)	P(1)−C(1)	1.815(3)	P(3)−C(13)	1.809(2)
P(2)−N(2)	1.603(2)	P(1)−C(19)	1.789(3)	P(3)−C(21)	1.792(3)
N(1)−P(1)−N(3)	116.8(1)	P(1)−N(1)−P(2)	121.8(1)	C(1)−P(1)−C(19)	104.4(1)
N(2)−P(2)−N(1)	117.1(1)	P(2)−N(2)−P(3)	121.2(1)	C(7)−P(2)−C(20)	103.6(1)
N(3)−P(3)−N(2)	116.8(1)	P(3)−N(3)−P(1)	121.0(1)	C(13)−P(3)− C(21)	104.4(1)
6b (Molecule 1)					
P(1)−N(1)	1.590(8)	P(3)−N(2)	1.597(8)	P(2)−C(7)	1.807(9)
P(1)−N(3)	1.613(8)	P(3)−N(3)	1.595(9)	P(2)−C(20)	1.779(11)
P(2)−N(1)	1.575(8)	P(1)−C(1)	1.796(10)	P(3)−C(13)	1.806(10)
P(2)−N(2)	1.602(8)	P(1)−C(19)	1.792(10)	P(3)−C(21)	1.811(9)
N(1)−P(1)−N(3)	116.5(4)	P(1)−N(1)−P(2)	124.7(5)	C(1)−P(1)−C(19)	105.4(5)
N(2)−P(2)−N(1)	116.3(4)	P(2)−N(2)−P(3)	122.5(5)	C(7)−P(2)−C(20)	103.6(5)
N(3)−P(3)−N(2)	118.0(4)	P(3)−N(3)−P(1)	121.5(5)	C(13)−P(3)− C(21)	102.1(5)
6b (Molecule 2)					
P(4)−N(4)	1.576(8)	P(6)−N(5)	1.579(8)	P(5)−C(37)	1.800(10)
P(4)−N(6)	1.616(7)	P(6)−N(6)	1.605(8)	P(5)−C(50)	1.765(10)
P(5)−N(4)	1.602(8)	P(4)−C(31)	1.817(9)	P(6)−C(43)	1.814(9)
P(5)−N(5)	1.618(7)	P(4)−C(49)	1.781(11)	P(6)−C(51)	1.781(10)
N(4)−P(4)−N(6)	117.6(4)	P(4)−N(4)−P(5)	123.6(5)	C(31)−P(4)− C(49)	105.0(5)
N(5)−P(5)−N(4)	115.9(4)	P(5)−N(5)−P(6)	122.8(5)	C(37)−P(5)− C(50)	104.5(5)
N(6)−P(6)−N(5)	117.9(4)	P(6)−N(6)−P(4)	120.9(5)	C(43)−P(6)− C(51)	102.6(5)

dissolved in CH_2Cl_2 and crystallized from a CH_2Cl_2–hexane solution to give colorless crystals of compound **5** (yield 85%).

Synthesis of [Me(Ph)PN]$_3$, 6. In a typical procedure, 15.15 g (43 mmol) of Me_3SiN═P(OPh)(Me)Ph was placed in a two-neck, 50 mL round-bottom flask equipped with a magnetic stir bar, a nitrogen inlet adapter, and a rubber septum. Freshly distilled 2,2,2-trifluoroethanol (0.525 mL, 6:1 molar ratio) was then added to the flask, and the mixture was allowed to stir for 2−4 days. The volatiles were removed from the resulting white slurry under vacuum (0.3 mmHg) at 110 °C. The residue was dissolved in ca. 150 mL of dichloromethane and then washed (3 × 15 mL) with aqueous KOH (1.4 M). Then dichloromethane was removed from the organic layer with a rotary evaporator, and the solid residue was further dried at 65 °C in a vacuum oven for 4 days. Both ^{1}H and ^{31}P NMR spectroscopy indicated that both the *cis* and the *trans* isomers were present in the oily residue and that no other cyclic species, e.g., tetramer, pentamer, etc., were formed. Yield: 6.41 g, 94%. A 3.91 g sample of the isomers of [Ph(Me)PN]$_3$ were separated using column chromatography [60 Å silica gel columns (25 × 250 mm) and elution with ethyl acetate]: *trans*, 2.89 g, 49%, R_f = 0.59; *cis*, 1.02 g, 17.5%, R_f = 0.15.

Cis Isomer 6a. ^{1}H NMR ($CDCl_3$): δ 1.80 (dt, 9 H, $^2J_{PH}$ = 14.2 Hz, $^4J_{PH}$ = 1.7 Hz), 7.60 (m, 6 H, C_6H_5), 7.27 (m, 3 H, C_6H_5), 7.17 (m, 6 H, C_6H_5). ^{13}C NMR{^{1}H} ($CDCl_3$): δ 24.0 (dt, P*Me*, J_{PC} = 101.1 Hz, $^3J_{PC}$ = 2.6 Hz), 127.7 (d, Ph, $C_{3,5}$, J_{PC} = 13.1 Hz), 129.5 (d, Ph, $C_{2,6}$, J_{PC} = 11.2 Hz), 130.1 (s, Ph, C_4), 138.6 (d, Ph, C_1, J_{PC} = 121.9 Hz). ^{31}P NMR{^{1}H} ($CDCl_3$): δ 19.6. IR (KBr pellet, cm^{-1}): 3074 w, 3051 w, 2984 m, 1481 m, 1439 m, 1412 m, 1292 s, 1186 vs, 1170 vs, 1119 s, 1026 w, 996 w, 925 m, 898 m, 884 s, 810 s, 759 m, 736 s, 722 s, 670 s, 687 s, 563 m, 508 m, 495 m, 446 s. Anal. Calcd for C_7H_8PN: C, 61.32, N, 10.21, H, 5.88. Found: C, 61.21, N, 9.98, H, 6.13. Mp: 156 °C.

Trans Isomer 6b. ^{1}H NMR ($CDCl_3$): δ 1.63 (d, 3 H, J_{PH} = 14.5 Hz), 1.67 (d, 6 H, J_{PH} = 14.0 Hz), 7.98 (m, 2H, C_6H_5), 7.72 (m, 4 H, C_6H_5), 7.46 (m, 3 H, C_6H_5), 7.29 (m, 6 H, C_6H_5). ^{13}C NMR{^{1}H} ($CDCl_3$): 22.9 (dt, P*Me*, J_{PC} = 102.1 Hz, $^3J_{PC}$ = 2.6 Hz), 23.1 (ddd, P*Me*, J_{PC} = 101.7 Hz, $^3J_{PC}$ = 3.6 Hz, $^3J_{PC}$ = 3.7 Hz), 127.8 (d, Ph, J_{PC} = 13.2 Hz), 128.1 (d, Ph, J_{PC} = 12.3 Hz), 129.5 (d, Ph, J_{PC} = 10.4 Hz), 129.6 (d, Ph, J_{PC} = 9.6 Hz), 130.2 (s, Ph), 130.4 (d, Ph, J_{PC} = 2.7 Hz), 138.8 (dd, Ph, J_{PC} = 121.7 Hz, $^3J_{PC}$ = 1.8 Hz), 139.5 (d, Ph, J_{PC} = 122.4 Hz). ^{31}P NMR{^{1}H} ($CDCl_3$): δ 20.3, 20.4. ^{1}H NMR (DMSO-d_6): δ 1.49 (d, 3 H, J_{PH} = 14.2 Hz), 1.54 (d, 6 H, J_{PH} = 14.2 Hz), 7.91 (m, 2H, C_6H_5), 7.72 (m, 4 H, C_6H_5), 7.51 (m, 3 H, C_6H_5), 7.38 (m, 6 H, C_6H_5). ^{31}P NMR{^{1}H} (DMSO-d_6): δ 18.1, 18.3. IR (KBr, pellet, cm^{-1}): 3070 w, 3053 m, 2977 m, 1478 w, 1437 m, 1416 m, 1408 m, 1291 s, 1183 vs, 1167 vs, 1120 s 1071 m, 1029 m, 997 w, 937 m, 897 m, 876 vs, 806 m, 789 s, 731 s, 719 m,, 696 s, 687 s, 511 s, 495 m, 465 s, 450 s. Anal. Calcd for C_7H_8PN: C, 61.32, N, 10.21, H, 5.88. Found: C, 61.21, N, 10.10, H, 6.13. Mp: 97 °C.

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Supporting Information Available: X-ray crystallographic files in CIF format for **6b**. This material is available free of charge via the Internet at http://pubs.acs.org. Compound **6a** has been deposited with the Cambridge Crystallographic Data Centre and is available as Deposit Number 157317.

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