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Isolation and Characterization of Nongeminal Cyclic Methylphenylphosphazene Tetramers

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Abstract: Heating pure samples of the cyclic phosphazenes, *cis*- or *trans*-$[Me(Ph)PN]_3$, yielded mixtures of the cis and trans isomers of the cyclic phosphazene trimers, $[Me(Ph)PN]_3$, and all four geometric isomers of the tetramers, $[Me(Ph)PN]_4$. Varying the temperature and heating times changes the ratio of these components. Following the thermolysis by NMR spectroscopy indicated that only a mixture of the two isomeric trimers occurred initially. Longer heating times produced mixtures of the isomers of the tetramer. Column chromatography and solubility differences were used to separate each of the isomers of the tetramer. Spectroscopic and X-ray crystallographic studies suggest that the four different geometrical isomers of the tetramer can be described as cone, partial cone, 1,2-alternate, and 1,3-alternate by analogy to calix[4]-arene.

Introduction

The inorganic heterocyclic compounds known as phosphazenes have long been studied as precursors to polymeric phosphazenes and for their facile substitution chemistry.[1,2] More recent attention has focused on a variety of uses of these compounds as cores in dendrimer synthesis,[3] as metal extraction systems,[4] and as channel-forming crystalline hosts for supporting novel species such as chains of I_2 molecules.[5] Among the most desirable features of the cyclic phosphazenes, $(R_2PN)_3$, are their unique shape and diverse chemistry which arise from an almost planar PN ring like benzene but with tetrahedral geometry and two substituents at each phosphorus. Recently we reported the preparation and isolation of the cis and trans isomers of unusual *nongeminally* substituted methyl phenyl cyclic phosphazenes, $[Me(Ph)PN]_3$,[6] and ethyl phenyl cyclic phosphazenes, $[Et(Ph)PN]_3$.[7] The synthetic method and the ability to isolate useful quantities of both the cis and trans isomers of these compounds provide access to new compounds with controlled stereochemistry and reactivity. In fact, the cis isomers have a basketlike shape analogous to the well-studied calixarenes[8] and cyclodextrins,[9] which have become increasingly important for molecular recognition, self-assembly of supramolecular structures, biological mimics, biological and chemical sensors, and hosts for metal catalysts and nanomaterials.[10] An important feature of the simple nongeminal methyl phenyl cyclics is that, by analogy to the well-studied polymer analogue, poly(methylphenylphosphazene),[11] the simple cis and trans isomers of $[Me(Ph)PN]_3$ are easily derivatized thus providing access to many new nongeminal cyclic phosphazenes with substituents that are attached by stable P−C bonds.

The analogous *nongeminally* substituted tetrameric cyclic phosphazenes present similarly interesting structural diversity. Among the earliest reports of nongeminally substituted tetramers was that of Shaw and co-workers,[2] which gave melting points for three of the four possible geometric isomers of $[Cl(Ph)PN]_4$, but made no structural assignments. Grushkin[12] and coworkers further studied this system and used ^1H NMR spectroscopy to identify three geometric isomers of the chloro

(1) For example, see: (a) Allcock, H. R. *Phosphorus−Nitrogen Compounds*; Academic Press: New York, 1972. (b) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315−356. (c) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119−135.
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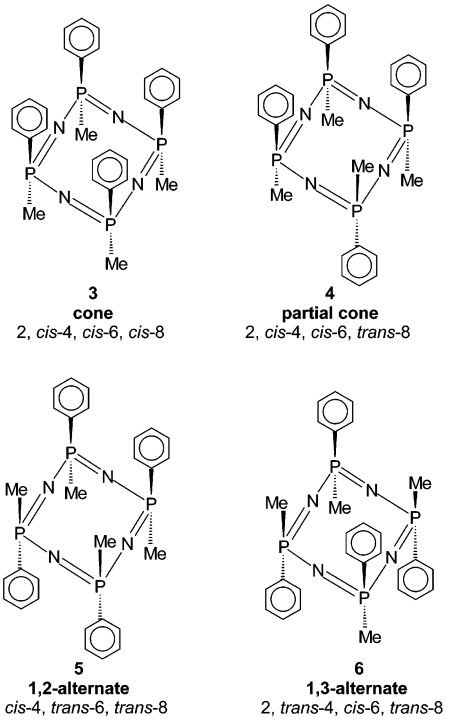
Chart 1



tetramer and two amino substituted derivatives. Since then, X-ray structural analyses of two geometric isomers of $[Cl(Ph)PN]_4$[13,14] have been reported, and there have been a few isolated reports of structural analysis of one or two geometric isomers of $[Ph(NHMe)PN]_4$[15] and $[Cl(NR_2)PN]_4$ (R = Me[16] or Et[17]). We have, however, found no study where all four geometric isomers of any *nongeminally* substituted tetrameric phosphazene have been isolated and characterized. Even more surprising is that, to our knowledge, there are no reports of the full structural characterization of all the geometric isomers of the isoelectronic, nongeminal cyclosiloxanes, particularly those with alkyl and aryl groups, i.e., $[Me(Ph)SiO]_4$.[18] We report herein the formation, isolation, and X-ray crystallographic characterization of all four geometric isomers of the novel nongeminal alkyl/aryl tetracyclophosphazene, $[Me(Ph)PN]_4$ (Chart 1).

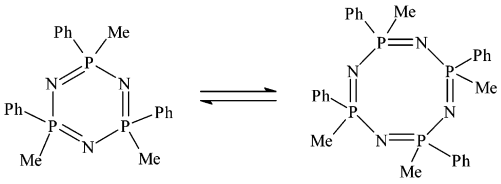
Although these types of isomers were originally referred to as *cis*, α-*trans*, *β*-*trans*, and *γ*-*trans*,[2,12] a more systematic naming system was developed.[13−15] For example, the full name for the cis isomer **3** is 2,*cis*-4,*cis*-6,*cis*-8-tetramethyl-2,3,4,5-tetraphenylcyclotetraphosphazene. The stereospecific part of each isomer name is a noted structure in Chart 1. By analogy to the calix[4]arene analogues, these isomers can also be described as cone, partial cone, 1,2-alternate, and 1,3-alternate isomers.

Table 1. NMR Study of Thermal Exchange of $[Ph(Me)PN]_3$ and $[Ph(Me)PN]_4$

temperature (°C)	heating time (day)	starting trimer	% cis trimer	% trans trimer	% tetramer
220	4	cis	39	57	4
		trans	12	87	1
	6	cis	41	54	6
		trans	18	76	6
	11	cis	20	68	12
		trans	18	69	13
250	5	cis	17	59	24
		trans	12	49	39
	7	cis	15	50	35
		trans	8	27	65
	12	cis	7	22	71
		trans	10	35	55

Results and Discussion

Synthesis of Methylphenylphosphazene Tetramers. Extensive studies of thermal ring expansion of cyclic phosphazenes have shown that easily ionizable substituents at phosphorus (e.g., halogens)[19] favor formation of high polymeric materials, while alkyl and aryl groups form exclusively small ring compounds.[20,21] Even when some halogen groups are present along with alkyl groups, these ring opening reactions still tend to form cyclic rather than polymeric compounds. Studies of the thermolysis of both $(Ph_2PN)_3$ and $(Me_2PN)_3$ have shown that cyclic trimers and tetramers exist in equilibrium when heated between 200 and 350 °C.[19,20] With the relatively recent availability of the cyclic trimers, *cis*- and *trans*-$[Me(Ph)PN]_3$, we were interested in using thermolysis reactions to obtain additional quantities of the basket-shaped cis trimer from the trans trimer. An added benefit of the thermolysis reactions was the formation of all four geometric isomers of the nongeminally substituted tetramer, $[Me(Ph)PN]_4$ (eq 1).



(1)

Thermal experiments were carried out at 220 and 250 °C in a temperature controlled oven using 20 mg samples of pure cis or trans isomers sealed in glass ampules. After periods of 4 to 12 days, the ampules were opened and the solid products were analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. This analysis was facilitated by a chemical shift difference of ca. 9 to 10 ppm between the trimers (cis δ 19.6, trans δ 18.1, 18.3) and the tetramers (δ ca. 10−11) which allowed quantifying the components by integration. In all cases, both isomers of the trimer, all four isomers of the tetramer, and trace quantities (<1%) of unidentified compounds, presumably higher cyclics, were present. As shown in Table 1, after heating at 220 °C for 4 to

(13) Bullen, G. J.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1651−1658.
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6 days, tetramers comprised less than 10% of the mixture. Even after 11 days, tetramers made up only 11 to 12%. However, at 250 °C, ca. 25 and 40% of the mixture were tetramers after only 5 days of heating the cis and trans isomers, respectively. This increased to as high as 71% after 12 days. The trans trimer was clearly favored over the cis trimer in all cases and usually reached a stable ratio of about 3.5 to 1 at 250 °C, regardless of whether the starting material was the cis or the trans trimer. Thus, ring opening does not appear to be a feasible way to acquire synthetically useful quantities of the cis isomer of the trimer from the trans isomer. Ring strain and steric effects are likely reasons that the cis trimer is more readily converted to the trans isomer. It is also interesting to note that, at the lower temperature and at shorter heating times, the isomerization of the trimers was more prevalent than the formation of tetramers, suggesting that isomerization occurs before ring expansion.

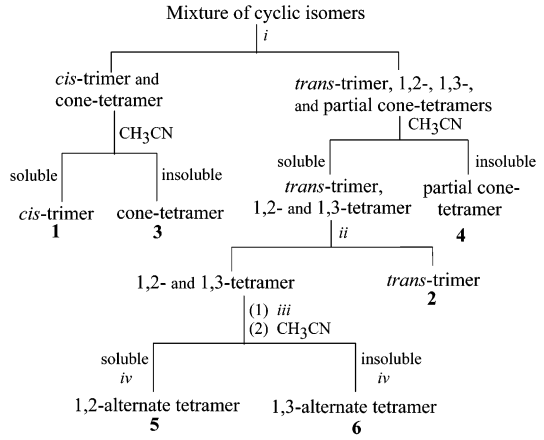
Pure samples of the cone and the partial cone isomers were also heated in sealed ampules. After 6 days at 250 °C, ^{31}P NMR spectroscopy indicated that all six isomers (two trimers and four tetramers) were present with an overall ratio of trimers: tetramers of ca. 20:80 in each case. Heating either the trimers or the tetramers between 280 and 300 °C for several days does not increase the amount of tetramers substantially; however, under such extreme conditions, degradation begins to occur and significant quantities (ca. 30 to 40%) of insoluble black solids formed.

Allcock and co-workers[19] have postulated a ring expansion mechanism for cyclic phosphazenes with electron releasing organic groups at phosphorus that involves heterolytic cleavage of the P−N bond to form a zwitterionic intermediate. This is favored by the enhanced electronegativity difference between the nitrogen and the phosphorus with electron releasing groups. Isomerization of the trimer can occur through reaction of the oppositely charged chain ends, while ring expansion occurs through reaction of the zwitterion with another ring followed by additional heterolytic bond cleavage and subsequent ring closure. Cyclization is favored over polymerization in either case due to the strong attraction between the polar chain ends.

Isolation and Characterization of Methylphenylphosphazene Tetramers. To isolate each of the four geometric isomers of the nongeminally substituted tetramers, 20.0 g of pure *trans*-[Me(Ph)PN]$_3$ were heated at 250 °C for 6 days in a large flask. On this scale, a ca. 63 to 37 ratio of trimers to tetramers was obtained as determined by ^{31}P NMR spectroscopy. The isolation of each of the components involved column chromatography and the differences in solubility of the isomers of the cyclic trimers and tetramers (Scheme 1).

Column chromatography with ethyl acetate as the eluent readily separated the cis trimer and cone tetramer from the various trans isomers. Although all the trimers and tetramers are very soluble in CH_2Cl_2, their solubility in acetonitrile is somewhat different, and this facilitated further separation after the initial chromatography. The cone and partial cone isomers are insoluble in cold CH_3CN, but both the cis and trans trimers are very soluble. Thus the cone tetramer, **3**, and the cis trimer, **1**, were easily separated in one additional step, and the partial cone-tetramer, **4**, was also readily isolated from the mixture of trans trimer, **2**, and 1,2- and 1,3-alternate tetramers, **5** and **6**. The trans trimer was then separated from the two remaining

Scheme 1 [a]



[a] (i) Column chromatography (ethyl acetate), (ii) column chromatography (ethyl acetate/hexanes = 1:1), (iii) HCl gas bubbled into ether solution to give white solids, (iv) extracted from 1.5 M aq KOH solution with CH_2Cl_2.

tetramers using column chromatography with a less polar eluent of a 1:1 mixture of ethyl acetate and hexanes.

Separation of the 1,2- and 1,3-alternate isomers was the most difficult because they have very similar solubilities. Nonetheless, the 1,2-alternate tetramer, **5**, is slightly less soluble in ether or hexane, and this difference facilitated the isolation of the pure 1,2-alternate tetramer. The 1,3-alternate tetramer, **6**, however, could not be obtained in pure form by fractional recrystallization. A better approach involved the preparation of the HCl adduct of the 1,2- and 1,3-alternate tetramers by bubbling HCl through an ether solution of the mixture of the two isomers. The adduct of the 1,2-alternate tetramer is soluble in CH_3CN, but the 1,3-alternate tetramer adduct is not. Once separated as adducts, the 1,2- and 1,3-alternate tetramers were easily recovered by dissolution into 1.5 M aqueous KOH to remove HCl. Subsequent extraction into CH_2Cl_2, solvent removal, and drying afforded pure samples of **5** and **6**. The overall yield of isolated cyclics was 84.5%, and the mass percentage composition was 17.7% *cis*-[Me(Ph)PN]$_3$, **1**; 53.2% *trans*-[Me(Ph)PN]$_3$, **2**; 3.6%, cone-[Me(Ph)PN]$_4$, **3**; 16.0% partial cone-[Me(Ph)PN]$_4$, **4**; 6.5% 1,2-alternate-[Me(Ph)PN]$_4$, **5**; and 3.0% 1,3-alternate-[Me(Ph)PN]$_4$, **6**.

Each of the geometric isomers of the tetramer were characterized by NMR and IR spectroscopy, elemental and thermal analyses, and X-ray crystallography. The phosphorus NMR spectra for **3**, **5**, and **6** exhibited just one signal at 11.7, 10.0, and 10.7 ppm, respectively. In addition to the aromatic resonances, the ^{1}H NMR spectra for **3**, **5**, and **6** contained a single doublet arising from the methyl group directly bonded to the phosphorus at 1.77 (J_{PH} = 12.4 Hz), 1.50 (J_{PH} = 12.6 Hz), and 1.42 (J_{PH} = 12.5 Hz) ppm, respectively. The simplicity of these spectra is due to the high symmetry of these molecules. Other the other hand, the ^{31}P NMR spectrum of **4** exhibited what is typically called an AB_2C pattern of three resonances, each of which appears as a triplet at 10.9 (J_{PP} = 7.5 Hz), 10.5 (J_{PP} = 7.1 Hz), and 10.2 (J_{PP} = 6.6 Hz) ppm and relative intensity 1:2:1.[22] The ^{1}H NMR spectrum for **4** contained three sets of doublets from the CH_3 protons directly bonded to the phosphorus at 1.31 (J_{PH} = 13.9 Hz), 1.62 (J_{PH} = 13.7 Hz), and

(22) Kumaraswamy, S.; Vijjulatha, M.; Muthiah, C.; KumaraSwamy, K. C.; Engelhardt, U. *J. Chem. Soc., Dalton Trans.* **1999**, 891−899.

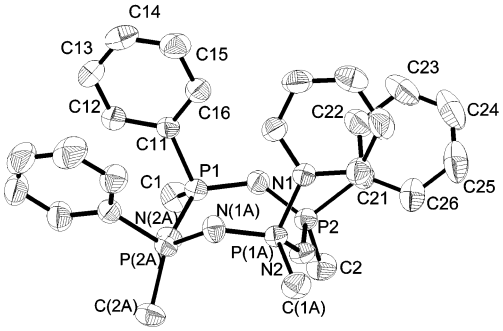


Figure 1. Thermal ellipsoid plot of **3**, cone-[Me(Ph)P═N]$_4$ (40% probability ellipsoids for non-hydrogen atoms are shown).

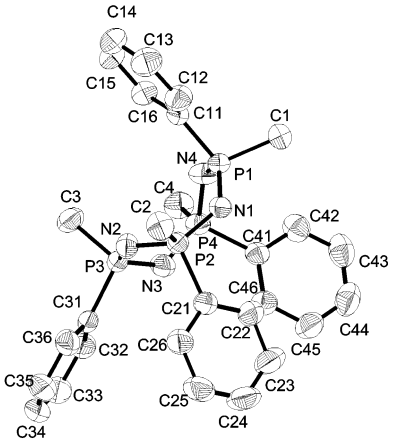


Figure 2. Thermal ellipsoid plot of **4**, partial cone-[Me(Ph)P═N]$_4$ (40% probability ellipsoids for non-hydrogen atoms are shown).

1.74 ppm (J_{PH} = 13.3 Hz) with an intensity distribution of 1:2:1, respectively. The ^{13}C NMR spectra clearly show all the short- and long-range couplings between phosphorus for the methyl carbons (i.e., doublets of triplets) and couplings between the carbons of the phenyl group and the nearest phosphorus nucleus. The characteristic strong band for the P−N stretching frequency at 1201, 1223, 1240, and 1252 cm^{-1} for **3**, **4**, **5**, and **6**, respectively, are clearly evident in the IR spectra.

Differential scanning calorimetry (DSC) data of each compound exhibited a sharp endothermic peak at 204, 152, 163, and 143 °C for **3**, **4**, **5**, and **6** which corresponds to the melting point (T_m) for each isomer. The cis isomer of the cyclic trimer, **1**, also had a significantly higher melting point (156 °C) than the trans isomer, **2** (97 °C**)**. These trends can be explained by intermolecular interactions and molecular packing. The DSC data for these new tetramers did not show any evidence of transitions indicative of thermal ring opening polymerization. Thermogravimetric analyses (TGA) data of the cyclic trimers and tetramers were similar with all six isomers showing a single one-step weight loss as expected for simple sublimation. There was essentially 100% weight loss by 600 °C for each isomer. Despite the slightly lower melting points of the various trans isomers **4**, **5**, and **6**, these isomers sublimed at temperatures 30 to 50 °C higher than the cis isomer **3** and the lower mass trimers.

Crystal Structures. The crystal structures of all four geometric isomers **3**, **4**, **5**, and **6** were determined by X-ray diffractometry (Figures 1−4). The crystal data are presented in Table 2, and selected bond distances and angles are given in Table 3. Isomer **3**, which formed orthorhombic crystals, has a 2-fold symmetry with a cone geometry that has all four phenyl

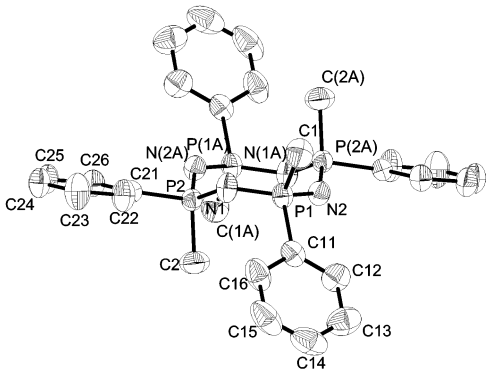


Figure 3. Thermal ellipsoid plot of **5**, 1,2-alternate [Me(Ph)P═N]$_4$ (40% probability ellipsoids for non-hydrogen atoms are shown).

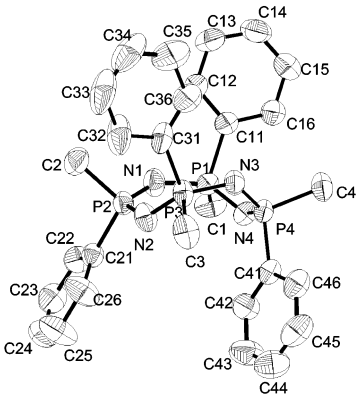


Figure 4. Thermal ellipsoid plot of **6**, 1,3-alternate [Me(Ph)P═N]$_4$ (40% probability ellipsoids for non-hydrogen atoms are shown).

Table 2. Crystal Data[a] for Cyclic Tetramers **3**, **4**, **5**, and **6**

compound	**3** (cone)	**4** (partial Cone)	**5** (1,2-alternate)	**6** (1,3-alternate)
empirical formula	$C_{28}H_{32}N_4P_4$	$C_{28}H_{32}N_4P_4$	$C_{28}H_{32}N_4P_4$	$C_{28}H_{32}N_4P_4$
formula weight	548.46	548.46	548.46	548.46
crystal system	orthorhombic	monoclinic	orthorhombic	triclinic
space group	*Pbcn*	$P2_1/c$	*Pbca*	$P\bar{1}$
a, Å	20.7790(10)	13.3078(6)	13.738(1)	9.2385(8)
b, Å	8.2761(5)	15.5628(7)	10.766(1)	10.6957(8)
c, Å	16.4341(9)	14.3446(7)	19.522(2)	16.4620(10)
α, deg	90	90	90	82.353(6)
β, deg	90	105.967(4)	90	84.901(7)
γ, deg	90	90	90	65.694(6)
V, Å^3	2826.2(3)	2856.2	2887.4(5)	1468.2(2)
Z	4	4	4	2
ρ_{cald} (g cm^{-1})	1.289	1.275	1.262	1.241
μ, mm^{-1}	0.292	0.289	0.285	0.281
extinction coefficient[31]	0.0063(12)	0.0008(7)	0.0025(7)	0.0009(4)
R1[b] [$I > 2\sigma(I)$]	0.036	0.041	0.041	0.043
wR2[b] [all data]	0.101	0.111	0.109	0.116

[a] Graphite monochromatized Mo Kα radiation, λ = 0.71 073 Å. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + F_o^2]/3$.

groups on the same side of the P_4N_4 ring. The partial cone isomer **4** crystallized in a monoclinic system and has three phenyl groups on one side of the P_4N_4 ring and one phenyl group on the opposite side of the ring. The centrosymmetric 1,2-alternate isomer **5** crystallized in an orthorhombic system, with two phenyl groups on the same side of the ring and on adjacent phosphorus atoms. Isomer **6** formed triclinic crystals and had a 1,3-alternate geometry as shown in Chart 1.

In general, the bond lengths in all the new nongeminal tetramer isomers are similar to closely related cyclic trimers

Table 3. Selected Bond Lengths and Angles for Cyclic Tetramers **3**, **4**, **5**, and **6**

	3	**4**	**5**	**6**
P(1)−N(1)	1.589(2)	1.592(2)	1.587(2)	1.589(2)
P(1)−N(4) or N(2A)	1.601(2)	1.595(2)	1.582(1)	1.586(2)
P(2)−N(1)	1.590(2)	1.599(2)	1.593(2)	1.574(2)
P(2)−N(2)	1.604(2)	1.598(2)	1.588(2)	1.590(2)
P(3)−N(2)		1.593(2)		1.584(2)
P(3)−N(3)		1.592(2)		1.594(2)
P(4)−N(3)		1.594(2)		1.596(2)
P(4)−N(4)		1.591(2)		1.588(2)
P(1)−C(1)	1.801(2)	1.799(3)	1.804(3)	1.797(3)
P(1)−C(11)	1.813(2)	1.819(2)	1.817(2)	1.813(3)
P(2)−C(2)	1.800(2)	1.793(3)	1.795(3)	1.799(3)
P(2)−C(21)	1.815(2)	1.812(2)	1.803(2)	1.812(3)
P(3)−C(3)		1.807(3)		1.793(3)
P(3)−C(31)		1.818(2)		1.814(3)
P(4)−C(4)		1.803(3)		1.800(3)
P(4)−C(41)		1.814(2)		1.812(3)
N(1)−P(1)−N(4) or N(2A)	119.3(1)	120.4(1)	121.2(1)	120.9(1)
N(2)−P(2)−N(1)	120.1(1)	119.2(1)	117.9(1)	121.7(1)
N(3)−P(3)−N(2)		120.4(1)		119.6(1)
N(4)−P(4)−N(3)		119.6(1)		119.6(1)
P(1)−N(1)−P(2)	133.9(1)	130.8(1)	132.6(1)	137.0(2)
P(2)−N(2)−P(3) or P(1A)	128.0(1)	129.7(1)	133.6(1)	133.1(2)
P(3)−N(3)−P(4)		129.6(1)		127.5(1)
P(4)−N(4)−P(1)		131.6(1)		132.9(1)
C(1)−P(1)−C(11)	105.7(1)	105.1(1)	104.0(1)	103.4(1)
C(2)−P(2)−C(21)	104.7(1)	105.9(1)	104.6(1)	103.7(1)
C(3)−P(3)−C(31)		103.8(1)		105.3(2)
C(4)−P(4)−C(41)		103.7(1)		106.1(1)

and tetramers, $(Me_2PN)_3$,[23] $(Ph_2PN)_3$,[24] *cis*- and *trans*-[Ph(Me)PN]$_3$,[6] *cis*- and *trans*-[Ph(Et)PN]$_3$,[7] and $(Me_2PN)_4$.[25] Average mean values of the P—N bond lengths for **3**, **4**, **5**, and **6** are 1.596(8) Å, 1.594(3) Å, 1.588(5) Å, and 1.588(7) Å, respectively. The P—aryl distances for **3** [mean 1.814(2) Å], **4** [mean 1.816(3) Å], **5** [mean 1.810(9) Å], and **6** [mean 1.813(1) Å] are close to the typical P—aryl distance of *cis*-[Ph(Me)PN]$_3$ [avg 1.811 Å], *trans*-[Ph(Me)PN]$_3$ [avg 1.807 Å],[6] and $(Ph_2P{=}N)_3$ [avg 1.804 Å].[24] The P—alkyl distances for **3** [mean 1.801(1) Å], **4** [mean 1.801(6) Å], **5** [mean 1.800(6) Å], and **6** [mean 1.798(3) Å] are also similar to other alkyl cyclics, $(Me_2P{=}N)_3$ [mean 1.810(10) Å],[23] $(Me_2P{=}N)_4$ [avg 1.805(4) Å],[25] *cis*-[Ph(Me)PN]$_3$ [mean 1.791(2) Å], *trans*-[Ph(Me)PN]$_3$ [mean 1.785(15) Å],[6] *cis*-[Ph(Et)PN]$_3$ [mean 1.798(5) Å], and *trans*-[Ph(Et)PN]$_3$ [mean 1.81(1) Å].[7]

The phosphazene ring in all four isomers is nonplanar as expected. With the exception of the 1,2-alternate isomer **5**, the PN ring is essentially a twisted saddle.[26−28] Isomer **5** has a chair conformation in which the six atoms P(1), N(1), N(2) and P(1A), N(1A), N(2A) are essentially coplanar. The other two atoms of the cyclic phosphazene ring, P(2) and P(2A), are on opposite sides of this plane with the distances +0.666 Å and −0.666 Å for P(2) and P(2A), respectively. This corresponds to the ring conformation in the 1,2-alternate isomers of [Cl(Ph)PN]$_4$[14] and its derivative [Ph(NHMe)PN]$_4$.[15] The N−P−N bond angles in all the isomers are typical of other phosphazene tetramers at 120° (119.3(1)° and 120.1(1)° in **3**, 119.2(1)°−120.4(1)° in **4**, 117.9(1)°−121.2(1)° in **5**, and 119.6(1)°−121.7(1)° in **6**). The P−N−P angles are ca. 131° (133.9(1)°−128.0(1)°) in **3**, 130° (129.6(1)°−131.6(1)°) in **4**, 133° (132.6(1)°−133.6(1)°) in **5**, and 133° (127.5(1)°−137.0(1)°) in **6**. The P−N−P angles of tetramers are about 10° larger than those observed in the analogous trimer [Ph(Me)PN]$_3$.[6] The exocyclic R−P−R bond angles are about 105° (105.7(1)°−104.7(1)°) in **3**, 105° (103.7(1)°−105.9(1)°) in **4**, in 104(1)° (104.0(1)°−104.6(1)°) in **5**, and 105° (103.4(1)°−106.1(1)°) in **6**.

Summary

The thermal ring opening reaction of the cis and trans isomers of the nongeminally substituted cyclic trimer, [Me(Ph)PN]$_3$, provides access to the first complete set of nongeminal tetrameric phosphazene rings. In the early stages of thermolysis, interconversion of the cis and trans trimers predominates, but at higher temperatures and longer reaction times, significant quantities of all four geometric isomers of the cyclic tetramers are formed. These new inorganic rings display interesting geometry and symmetry, and the enhanced basicity of the lone pairs of electrons on nitrogen should make these cyclic phosphazene tetramers unusual ligands. Structural studies suggest that π bonding plays a partial role in the formation of metal carbonyl[29] and platinum[30] complexes of related cyclophosphazenes, $[Me_2PN]_4$ and $[(MeNH)_2PN]_4$. Thus, metal complexes of this set of four isomers could produce complexes with unusual geometries and should shed considerable light on the bonding modes between the metal and nitrogen atoms in the ring.

Experimental Section

Hexanes and diethyl ether were distilled from CaH_2 and Na/benzophenone, respectively. Anhydrous HCl was used as received from Matheson, and the trimers [(Ph)MePN]$_3$ were prepared by published procedures.[6] The cyclic phosphazene products were handled in the atmosphere. For chromatography separations, 60 Å 230−400 mesh silica gel was used. NMR spectra were recorded on an SGI/Bruker DRX-400 spectrometer using $CDCl_3$ as a solvent. Positive ^{1}H 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 and IR spectra were obtained on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106 and a Nicolet 560 IR spectrometer, respectively. Thermogravimetric analysis data and differential scanning calorimetry were done under a nitrogen atmosphere using TA instruments SDT 2960 and DSC 2010 modules operating from room temperature to 800 °C and to 350 °C, respectively.

X-ray Crystallography. The diffraction data were collected at room temperature on a Bruker P4 diffractometer with Mo Kα radiation, λ = 0.710 73 Å. The pertinent crystallographic data are summarized in Table 2. Crystals for analyses of **3** (colorless flat slab), **4** (colorless plates), **5** (colorless plates), and **6** (colorless plates) were grown from saturated ethyl acetate solutions. The crystals were manipulated under air during the mounting procedure. The four structures were solved by direct methods and subsequent difference Fourier syntheses using the *SHELXTL-Plus* package.[31] All structures were refined by full-matrix least-squares methods against F^2 (SHELX97).[32] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were constrained

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with a riding model. Selected bond distances and angles are listed in Table 3. 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.

Thermal Experiments. Glass ampules that had been washed with deionized water and acetone and dried in an oven were charged with ca. 20 mg of trimer, [(Ph)MePN]$_3$, or tetramer, [(Ph)MePN]$_4$. The ampules were then sealed under vacuum and heated at 220 or 250 °C in a temperature-controlled oven for 4 to 12 days. The ampules were cooled to room temperature and then opened. The solid products were removed by dissolving in $CDCl_3$ and analyzed by NMR spectroscopy. Relative percentages of the cis and trans trimers are based on integration of $^{31}P\{^1H\}$ NMR spectra taking into account that there are three and four atoms of phosphorus in the trimers and tetramers, respectively. The data for heating the cyclic trimers are shown in Table 1. After heating for 6 days at 250 °C, the cone tetramer gave a mixture of trimers/tetramers in a 20:80 ratio and the partial cone tetramer gave a ratio of 22:78. All six geometric isomers of the trimers and tetramers were present.

Large Scale Preparation and Separation. A 20.0 g sample of the pure trans isomer, **2**, was placed in a 500 mL round-bottom flask equipped with a nitrogen inlet adapter. The flask was evacuated, then filled with nitrogen, and finally placed in a 250 °C sand bath for 6 days. After cooling to room temperature, the solid products were removed by dissolution in CH_2Cl_2. Upon solvent removal, the mixtures of isomers were analyzed by $^{31}P\{^1H\}$ NMR spectroscopy which indicated a trimer/tetramer ratio of 67:33. The mixture was further purified by a combination of column chromatography and solubility differences in CH_3CN (Scheme 1). First column chromatography (silica gel with ethyl acetate) was used to separate a mixture of **1** and **3** from a mixture of **2**, **4**, **5**, and **6**. R_f values in ethyl acetate are 0.15, 0.25, 0.59, 0.85, 0.89, and 0.87 for **1**, **2**, **3**, **4**, **5**, and **6**, respectively. The cis trimer, **1**, and cone tetramer, **3**, were separated by their different solubilities in CH_3CN, and **4** was also separated from **2**, **5**, and **6** in the same manner. Column chromatography on the mixture of **2**, **5**, and **6** using 1:1 ethyl acetate/hexanes successfully separated the trans trimer, **2**. R_f values were 0.37, 0.71, and 0.76 for *trans*-[Ph(Me)PN]$_3$, **2**, 1,2-alternate [Ph(Me)PN]$_4$, **5**, and 1,3-alternate [Ph(Me)PN]$_4$, **6**, respectively. The mixture of **5** and **6** was dissolved in ether, and then anhydrous HCl was bubbled through the solution until no more precipitation was observed. The precipitate was isolated and dried under vacuum. Then CH_3CN was added. The insoluble adduct of **6** was collected by filtration, and the soluble adduct of **5** was isolated by removal of solvent from the filtrate. Each of these components was dissolved in 1.5 M aq KOH, and this solution was extracted with CH_2Cl_2 to yield pure 1,2-alternate isomer, **5**, and 1,3-alternate isomer, **6**. All products were dried under vacuum at room temperature. The trimers, **1** and **2**,[6] and all the geometric isomers of the tetramers were characterized by NMR spectroscopy. Final isolated yields were *trans*-[Me(Ph)PN]$_3$ (9.0 g), *cis*-[Me(Ph)PN]$_3$ (3.0 g), cone-[Me(Ph)PN]$_4$ (0.6 g), partial cone-[Me(Ph)PN]$_4$ (2.7 g), 1,2-alternate-[Me(Ph)PN]$_4$ (1.1 g), and 1,3-alternate-[Me(Ph)PN]$_4$ (0.5 g).

Cone Isomer of [Me(Ph)P═N]$_4$, 3. ^1H NMR ($CDCl_3$): δ 1.77 (d, 12 H, PCH_3, J_{PH} = 12.4 Hz), 7.10 (t, 8 H, C_6H_5, J_{PH} = 6.7 Hz), 7.22 (t, 4 H, C_6H_5, J_{PH} = 6.4 Hz), 7.50 (dd, 8 H, C_6H_5, J_{PH} = 12.0 Hz, J_{PH} = 7.4 Hz). ^{13}C NMR$\{^1H\}$ ($CDCl_3$): δ 22.7 (d, PCH_3, J_{PC} = 100.5 Hz), 127.1 (d, Ph, J_{PC} = 12.7 Hz), 129.3 (s, Ph), 130.1 (m, Ph), 137.3 (d, Ph, J_{PC} = 124.3 Hz). ^{31}P NMR$\{^1H\}$ ($CDCl_3$): δ 10.7. IR (KBr, pellet, cm^{-1}): 3071 m, 3058 m, 3051 m, 3008 m, 2981 m, 2974 m, 1480 w, 1435 m, 1413 w, 1297 s, 1256 s, 1201 vs, 1171 s, 1118 s, 1027 w, 951 s, 891 s, 879 s, 871 s, 802 s, 788 m, 741 s, 715 s, 693 s, 669 m, 654 m, 561 m, 521 m, 493 s, 459 m. Anal. Calcd for $C_{28}H_{32}P_4N_4$: C, 61.32; N, 10.21; H, 5.88. Found: C, 60.44; N, 9.91; H, 5.99. Mp 204.1 °C; T_{50} (50% weigh loss) 320 °C.

Partial Cone Isomer of [Me(Ph)P═N]$_4$, 4. ^1H NMR ($CDCl_3$): δ 1.31 (d, 3 H, PCH_3, J_{PH} = 13.9 Hz), δ 1.62 (d, 6 H, PCH_3, J_{PH} = 13.7 Hz), δ 1.74 (d, 3 H, PCH_3, J_{PH} = 13.3 Hz), 7.17 (m, 2 H, C_6H_5), 7.27 (m, 5 H, C_6H_5), 7.34 (m, 2 H, C_6H_5), 7.43 (m, 3 H, C_6H_5), 7.69 (m, 2 H, C_6H_5), 7.76 (m, 4 H, C_6H_5), 8.01 (m, 2 H, C_6H_5). ^{13}C NMR$\{^1H\}$ ($CDCl_3$): δ 21.9 (td, PCH_3, J_{PC} = 97.6 Hz, $^3J_{PC}$ = 5.0 Hz), 22.7 (PCH_3, J_{PC} = 100.1 Hz, $^3J_{PC}$ = 2.5 Hz), 23.1 (PCH_3, J_{PC} = 103.4 Hz, $^3J_{PC}$ = 2.0 Hz), 127.2 (d, Ph, J_{PC} = 12.6 Hz), 127.4 (d, Ph, J_{PC} = 12.5 Hz), 127.8 (d, Ph, J_{PC} = 12.4 Hz), 129.3 (d, Ph, J_{PC} = 2.3 Hz), 129.6 (d, Ph, J_{PC} = 1.9 Hz), 129.9 (d, Ph, J_{PC} = 2.4 Hz), 130.1 (d, Ph, J_{PC} = 10.0 Hz), 130.2 (d, Ph, J_{PC} = 9.8 Hz), 130.3 (d, Ph, J_{PC} = 10.1 Hz), 138.0 (d, Ph, J_{PC} = 131.4 Hz, $^3J_{PC}$ = 5.1 Hz), 138.5 (d, Ph, J_{PC} = 127.5 Hz, $^3J_{PC}$ = 5.7 Hz), 139.3 (d, Ph, J_{PC} = 127.4 Hz, $^3J_{PC}$ = 6.5 Hz). ^{31}P NMR$\{^1H\}$ ($CDCl_3$): δ 10.22 (t, J_{PP} = 6.6 Hz), 10.47 (t, J_{PP} = 7.1 Hz), 10.92 (t, J_{PP} = 7.5 Hz). IR (KBr, pellet, cm^{-1}): 3073 m, 3054 m, 3007 m, 2982 m, 2908 m, 1479 m, 1437 s, 1411 m, 1298 s, 1223 vs, 1173 s, 1115 s, 1027 m, 953 m, 882 s, 802 s, 789 m, 762 m, 745 s, 719 s, 695 s, 667 s, 524 s, 507 m, 490 m, 471 s, 455 s. Anal. Calcd for $C_{28}H_{32}P_4N_4$: C, 61.32; N, 10.21; H, 5.88. Found: C, 61.41; N, 10.23; H, 6.00. Mp 152 °C; T_{50} 368 °C.

1,2-Alternate Isomer of [Me(Ph)P═N]$_4$, 5. ^1H NMR ($CDCl_3$): δ 1.50 (d, 12 H, PCH_3, J_{PH} = 12.6 Hz), 7.32 (m, 12 H, C_6H_5), 7.88 (m, 8 H, C_6H_5). ^{13}C NMR$\{^1H\}$ ($CDCl_3$): δ 22.6 (td, PCH_3, J_{PC} = 98.5 Hz, $^3J_{PC}$ = 2.9 Hz), 127.5 (t, Ph, J_{PC} = 6.4 Hz), 129.6 (s, Ph), 130.2 (t, Ph, J_{PC} = 5.4 Hz), 138.8 (md, Ph, J_{PC} = 129.2 Hz). ^{31}P NMR$\{^1H\}$ ($CDCl_3$): δ 10.0. IR (KBr, pellet, cm^{-1}): 3071 m, 3054 m, 3033 m, 3008 m, 2979 m, 2909 m, 1478 m, 1437 s, 1407 m, 1292 s, 1258 s, 1250 s, 1240 vs, 1176 s, 1117 s, 1067 m, 1029 m, 999 m, 912 m, 877 s, 798 s, 751 s, 718 s, 692 s, 662 s, 519 s, 500 m, 472 s, 426 m. Anal. Calcd for $C_{28}H_{32}P_4N_4$: C, 61.32; N, 10.21; H, 5.88. Found: C, 61.73; N, 10.08; H, 6.17. Mp 163 °C; T_{50} 352 °C.

1,3-Alternate Isomer of [Me(Ph)P═N], 6. ^1H NMR ($CDCl_3$): δ 1.42 (d, 12 H, PCH_3, J_{PH} = 12.5 Hz), 7.42 (m, 12 H, C_6H_5), 7.95 (m, 8 H, C_6H_5). ^{13}C NMR$\{^1H\}$ ($CDCl_3$): δ 22.2 (td, PCH_3, J_{PC} = 99.5 Hz, $^3J_{PC}$ = 3.1 Hz), 127.7 (t, Ph, J_{PC} = 6.3 Hz), 129.8 (s, Ph), 130.3 (t, Ph, J_{PC} = 5.0 Hz), 139.2 (md, Ph, J_{PC} = 128.0 Hz). ^{31}P NMR$\{^1H\}$ ($CDCl_3$): δ 11.7. IR (KBr, pellet, cm^{-1}): 3071 m, 3048 m, 3034 m, 3009 m, 2983 m, 2911 m, 1480 m, 1438 s, 1412 m, 1296 s, 1251 vs, 1203 s, 1168 s, 1117 s, 1028 m, 949 m, 877 s, 793 m, 738 s, 694 m, 665 s, 524 s, 508 m, 474 s, 452 s. Anal. Calcd for $C_{28}H_{32}P_4N_4$: C, 61.32; N, 10.21; H, 5.88. Found: C, 61.79; N, 10.23; H, 6.09. Mp 143 °C; T_{50} 372 °C.

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Supporting Information Available: X-ray crystallographic files in CIF format for **3**, **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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