Oxidative Addition of Tetrachloro-1,2-benzoquinone to λ^3-Cyclotriphosphazanes. An Unusual Ring Contraction−Rearrangement

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The λ^3-cyclotriphosphazanes, $[EtNP(OR)]_3$ [R = 2,6-$Me_2C_6H_3$ (**1**), 4-BrC_6H_4 (**2**), or CH_2CF_3(**3**)], on treatment with tetrachloro-1,2-benzoquinone (TCB) give the λ^5-cyclodiphosphazanes, $[EtNP(O_2C_6Cl_4)(OR)][EtNP(O_2C_6Cl_4)\{N(Et)P(OR)_2\}]$ (**5**−**7**) by an unusual ring contraction−rearrangement. The reaction of the mixed substituent λ^3-cyclotriphosphazane, $[(EtN)_3P_3(OR)_2(OR')]$ [R = 2,6-$Me_2C_6H_3$, R′ = 4-BrC_6H_4] (**4**), with TCB gives the λ^5-cyclodiphosphazane, $[EtNP(O_2C_6Cl_4)(OR')][EtNP(O_2C_6Cl_4)\{N(Et)P(OR)_2\}]$ (**8**), in which 4-bromophenoxide resides on one of the ring phosphorus atoms. The λ^3-bicyclic tetraphosphapentazane, $(EtN)_5P_4(OPh)_2$, on treatment with TCB undergoes a double ring contraction−rearrangement to give the λ^5-cyclodiphosphazane, $(EtN)[(EtN)_2P_2(O_2C_6Cl_4)_2(OPh)]_2$ (**9**). Variable-temperature and high-field ^{31}P NMR studies indicate the presence of more than one isomer in solution for the rearranged products **5**−**9**. The solid state structure of **8** reveals a trans arrangement of the substituents with respect to the P_2N_2 ring in contrast to the gauche arrangement observed for **5**.

Introduction

The chemistry of phosphorus−nitrogen compounds containing pentacoordinated phosphorus is interesting not only from their structural aspects but also from their dynamic behavior in solution manifested by pseudorotation, apical−equatorial exchange, and geometrical isomerism.[1] Schmutzler and co-workers have studied the reaction of six-membered 1,5,2,4-diazadiphosphorinan-6-one with tetrachloro-1,2-benzoquinone (TCB) to give products in which the ring is either retained[2a] or transformed to give ring-contracted products[2b] depending upon the nature of the substituents on the phosphorus atoms. As λ^3-cyclotriphosphazanes, $[EtNP(OR)]_3$ [R = 2,6-$Me_2C_6H_3$ (**1**), 4-BrC_6H_4 (**2**), or CH_2CF_3 (**3**)], possess three tricoordinated phosphorus centers, they would be good starting materials for the above-mentioned reactions. We had reported in a communication that the reaction of λ^3-cyclotriphosphazanes **1** or **2** with TCB gives λ^5-cyclodiphosphazanes $[EtNP(O_2C_6Cl_4)(OR)][EtNP(O_2C_6Cl_4)\{N(Et)P(OR)_2\}]$ **5** or **6** by an unusual ring contraction−rearrangement.[3] Herein, we present a detailed study of the above rearrangement along with the synthesis of a mixed substituent λ^3-cyclotriphosphazane, $[(EtN)_3P_3(OR)_2(OR')]$ [R = 2,6-$Me_2C_6H_3$, R′ = 4-BrC_6H_4] (**4**), and its reaction with TCB. Also included in this study is the reaction of λ^3-bicyclic tetraphosphapentazane, $(EtN)_5P_4(OPh)_2$, with TCB.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk-line techniques.[4] Solvents were purified by standard procedures and freshly distilled prior to use.[5] The cyclotriphosphazanes $[EtNPX]_3$ [X = Cl, O-2,6-$Me_2C_6H_3$ (**1**), O-4-BrC_6H_4 (**2**), or OCH_2CF_3 (**3**)][6,7a] and the bicyclic tetraphosphapentazane $(EtN)_5P_4(OPh)_2$[8] were synthesized by the literature procedures. Tetrachloro-1,2-benzoquinone (Aldrich) was used as purchased. IR spectra were recorded in KBr disks using a Bio-Rad FTIR spectrometer. The ^1H, ^{13}C ($SiMe_4$, internal standard), and ^{31}P (85% H_3PO_4, external standard) NMR spectra were recorded in $CDCl_3$ employing a Bruker AMX 400 or ACF-200 spectrometer. The $^{31}P-^{31}P$ COSY NMR spectrum was recorded in CD_2Cl_2 employing a Bruker DRX 600 spectrometer. Chemical shifts downfield from the standard were assigned positive values. Mass spectra were recorded with either a JEOL MS-DX 303 or Finnigan Mat 8230 (FAB) spectrometer.

Synthesis of Cyclotriphosphazane 4. Chlorocyclotriphosphazane $[EtNPCl]_3$ (6.00 g, 0.02 mol) in CH_2Cl_2 (25 mL) was added dropwise over a period of 15 min to a solution of the sodium salt of 2,6-dimethylphenol [prepared from 2,6-dimethylphenol (4.46 g, 0.04 mol) and NaH (0.80 g) in THF (30 mL)]. The reaction mixture was stirred for 4 h, and the sodium salt of 4-bromophenol [prepared from 4-bromophenol (3.16 g, 0.02 mol) and NaH (0.48 g) in THF (20 mL)] was slowly added to the above mixture. Stirring was continued for 24 h. The reaction mixture was filtered to remove NaCl, and solvent was evaporated under reduced pressure to give a cis−trans isomeric mixture of **4** as a viscous oil. Yield: 5.80 g (50%). Satisfactory C, H, N analysis could not be obtained for **4** because of its high sensitivity to air and moisture. ^{31}P NMR: cis δ 96.7 (1 P), 98.2 (2 P); trans 123.9 (1 P),

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Table 1. ^{31}P NMR Data for Cyclodiphosphazanes **5**−**8**

compd	chemical shift, ppm δ_A	δ_M	δ_X	coupling constant, Hz $^2J_{AM}$	$^2J_{MX}$
5					
isomer **C**[a]	−52.8	−46.3	142.8	166.8	81.5
isomer **D**	−54.9	−45.2	140.3	164.1	99.0
6					
isomer **C**[a]	−53.8	−47.8	140.3	160.4	91.9
isomer **D**	−55.0	−46.8	140.4	162.9	91.1
7[b]					
isomer **C**[a]	−50.4	−46.5	157.2	163.7	96.4
isomer **D**	−50.8	−45.6	157.2	165.3	90.0
isomer **E**	−48.2	−46.1	157.5	159.7	90.9
isomer **F**	−49.6	−45.6	157.7	161.0	90.8
8					
isomer **C**[a]	−53.1	−47.1	141.3	164.1	95.5
isomer **D**	−54.1	−47.4	143.0	166.8	83.7

[a] Major isomer (gauche) as judged from the relative intensities of the resonances. [b] $^4J_{AX}$ = 2, 0, 4, and 2 Hz for isomers **C**, **D**, **E**, and **F** of **7**. $^4J_{AX}$ = 0 Hz for **5**, **6**, and **8**.

127.1 (2 P). $^2J_{PP} \sim 0$ Hz. Mass spectrum (EI, ^{79}Br): no molecular ion found; other peaks observed at *m*/*z* 514 [M − $OC_6H_3Me_2$], 464 [M − OC_6H_4Br], 319 [M − {2 ($OC_6H_3Me_2$), 2 Et, Me, H}], and 269 $[(EtN)_2P_2(OC_6H_3Me_2)]^+$ with the expected bromine isotopic pattern.

Synthesis of Cyclodiphosphazanes 5, 6,[3] 7 and 8. A solution of cyclotriphosphazane **1** (0.73 g, 1.25 mmol) in CH_2Cl_2 (10 mL) was slowly added in drops to TCB (0.61 g, 2.50 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was warmed to 25 °C and stirred for 24 h. Solvent was removed under reduced pressure; the residue was washed with cold petroleum ether (bp 60−80 °C) to remove unreacted **1**. The petroleum ether insoluble material was crystallized from toluene to obtain colorless crystals of **5**. Yield: 0.74 g (55%). When the reaction was carried out using 1:1 stoichiometry of **1** and TCB, **5** was isolated in 30% yield (0.40 g) along with unreacted **1**. Analogous to the preparation of **5**, compounds **6**−**8** were prepared from **2**−**4** and TCB in a 1:2 molar ratio. Reaction of **1** or **2** with TCB in a 1:3 molar ratio gave **5** or **6** and unreacted TCB. However, the reaction of **3** with TCB in a 1:3 molar ratio gave an intractable mixture of products. The solvents used for the crystallization of **6**, **7**, and **8** were 1,2-dichlorobenzene, benzene−methanol (10:1), and toluene, respectively. The yield, melting point, microanalyses, and selected IR and NMR data are given below. The ^{31}P NMR data are summarized in Table 1.

Compound 5. Mp: >210 °C. Anal. Calcd for $C_{42}H_{42}Cl_8N_3O_7P_3$: C, 46.82; H, 3.93; N, 3.90. Found: C, 47.14; H, 3.96; N, 3.81. IR [ν(asym)PNP]: 896 (s), 867 (vs), 847 (s), 815 (s) cm^{-1}. For the details of ^{1}H NMR data, see ref 3. ^{13}C NMR: isomer **C** (see Figure 2), δ 15.86 (s, 3 C, exocyclic NCH_2CH_3), 16.37 (s, 6 C, ring NCH_2CH_3), 17.80, 17.86 (s, 2 C, CH_3, λ^3-P Ar), 18.73 (s, 12 C, CH_3, λ^5-P Ar, isomers **C** and **D**), 39.37 (s, 1 C, exocyclic NCH_2CH_3), 39.56 (s, 2 C, ring NCH_2CH_3); isomer **D** (see Figure 2), δ 16.60 (s, 1 C, exocyclic NCH_2CH_3), 16.92 (s, 2 C, ring NCH_2CH_3), 17.60, 17.68 (s, 2 C, CH_3, λ^3-P Ar), 38.24 (s, 1 C, exocyclic NCH_2CH_3), 39.31 (s, 2 C, ring NCH_2CH_3), 114.48, 124.12, 124.28, 124.49, 124.74, 124.88, 128.84, 129.08, 129.15, 129.60, 130.03, 130.24, 140.67, 140.93 and 149.52 (aryl carbon nuclei for isomers **C** and **D**).

Compound 6. Yield: 60%. Mp: >210 °C. Anal. Calcd for $C_{36}H_{27}Br_3Cl_8N_3O_7P_3$: C, 35.16; H, 2.21; N, 3.42. Found: C, 34.73, H, 2.33; N, 3.39. IR [ν(asym)PNP]: 900 (vs), 873 (s), 859 (s), 840 (vs), 820 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$ and 1,2-$Cl_2C_6H_4$): isomer **C**, δ 1.30 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, ring NCH_2CH_3), 1.33 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, exocyclic NCH_2CH_3), 2.94 (br, 4 H, ring NCH_2CH_3), 3.45 (br, 2 H, exocyclic NCH_2CH_3), 7.18−7.40 (m, 24 H, aryl protons for isomers **C** and **D**); isomer **D**, δ 1.17 (t, $^3J_{HH}$ = 6.90 Hz, 6 H, ring NCH_2CH_3), 1.37 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, exocyclic NCH_2CH_3), 3.10 (br, 4 H, ring NCH_2CH_3), 3.65 (br, 2 H, exocyclic NCH_2CH_3).

Compound 7. Yield: 51%. Mp: 210 °C. Anal. Calcd for $C_{24}H_{21}Cl_8F_9N_3O_7P_3$: C, 28.51; H, 2.09; N, 4.16. Found: C, 28.52; H, 2.76; N, 4.45. IR [ν(asym)PNP]: 901 (vs), 839 (vs), 819 (s) cm^{-1}.

Compound 8. Yield: 60%. Mp: 210 °C. Anal. Calcd for $C_{40}H_{37}BrCl_8N_3O_7P_3$: C, 42.59; H, 3.31; N, 3.72. Found: C, 42.85; H, 3.34; N, 3.56. IR [ν(asym)PNP]: 900 (vs), 875 (m), 860 (vs), 830 (vs), 815 (vs) cm^{-1}. ^{1}H NMR: isomer **C**, δ 1.25 (t, $^3J_{HH}$ = 6.9 Hz, 6 H, ring NCH_2CH_3), 1.39 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, exocyclic NCH_2CH_3), 2.06 (s, 12 H, CH_3, λ^3-P Ar), 3.05 (br, 4 H, ring NCH_2CH_3), 3.60 (br, 2 H, exocyclic NCH_2CH_3), 6.70−7.28 (m, 20 H, aryl protons for isomers **C** and **D**); isomer **D**, δ 1.17 (t, 6 H, $^3J_{HH}$ = 6.90 Hz, ring NCH_2CH_3), 1.54 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, exocyclic NCH_2CH_3), 2.19 (s, 12 H, CH_3, λ^3-P Ar), 3.20 (br, 4 H, ring NCH_2CH_3), 3.85 (br, 2 H, exocyclic NCH_2CH_3).

Synthesis of Cyclodiphosphazane 9. The bicyclic tetraphosphapentazane $(EtN)_5P_4(OPh)_2$ (1.30 g) admixed with a small amount of cyclotriphosphazane $[EtNP(OPh)]_3$ in toluene (10 mL) was slowly added over a period of 15 min to a solution of TCB (0.61 g) in toluene (20 mL) at 0 °C. The reaction mixture was brought to 25 °C and stirring continued for 12 h. The ^{31}P NMR spectrum of the reaction mixture indicated substantial amounts of tetracoordinated phosphorus compounds and a small amount of $(EtN)[(EtN)_2P_2(O_2C_6Cl_4)_2(OPh)]_2$ (**9**) along with traces of the cyclodiphosphazane, $[EtNP(O_2C_6Cl_4)(OPh)]$-$[EtNP(O_2C_6Cl_4)\{N(Et)P(OPh)_2\}]$. The reaction mixture was passed through a short silica gel column and eluted with toluene to remove tetracoordinated phosphorus compounds. Removal of the solvent under reduced pressure gave a colorless pasty mass, which was dissolved in 20 mL of a toluene−petroleum ether mixture (1:1). Slow evaporation of the solvent at 25 °C resulted in the deposition of **9** (1.0 g) as a colorless solid. Mp: 160 °C. Anal. Calcd for $C_{46}H_{35}Cl_{16}N_5O_{10}P_4$: C, 36.62; H, 2.34; N, 4.64. Found: C, 36.10; H, 2.69; N, 4.90. Mass spectrum (FAB, ^{35}Cl): *m*/*z* 1501 [M$^+$]. Other prominent peaks were observed at 984 [M − {2 ($O_2C_6Cl_4$), Et}], 891 [M − {2 ($O_2C_6Cl_4$), Et, OPh}], 772 $[(EtN)_3P_2(O_2C_6Cl_4)_2(OPh)]$, 729 $[(EtN)_2P_2(O_2C_6Cl_4)_2(OPh)]$, 679 $[(EtN)_3P_2(O_2C_6Cl_4)_2]$, 528 $[(EtN)_3P_2(O_2C_6Cl_4)(OPh)]$, and 485 $[(EtN)_2P_2(O_2C_6Cl_4)(OPh)]$ with the expected chlorine isotopic pattern. IR [ν(asym)PNP]: 822 (vs), 900 (vs) cm^{-1}. ^{31}P NMR: AB pattern, isomer **G** (gauche−gauche, major), δ_A −54.8, δ_B −52.0; $^2J_{AB}$ = 148.8 Hz; isomer **H** (trans−trans, minor), δ_A −55.0 and δ_B −51.6; $^2J_{AB}$ = 151.2 Hz. ^{1}H NMR: isomer **G** (gauche−gauche), δ 1.14 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, exocyclic NCH_2CH_3), 1.41 (t, $^3J_{HH}$ = 6.9 Hz, 12 H, ring NCH_2CH_3), 2.66 (m br, 4 H, exocyclic NCH_2CH_3, isomers **G** and **H**), 3.08 (m br, 8 H, ring NCH_2CH_3), 6.93−7.38 (m, 12 H, phenyl protons, isomers **G** and **H**); isomer **H** (trans−trans), δ 1.18 (t, $^3J_{HH}$ = 7.9 Hz, 3 H, exocyclic NCH_2CH_3), 1.23 (t, $^3J_{HH}$ = 6.8 Hz, 12 H, ring NCH_2CH_3), 3.23 (m br, 8 H, ring NCH_2CH_3). ^{13}C NMR: isomer **G** (gauche−gauche), δ 16.97 (s, 4 C, ring NCH_2CH_3), 18.23 (s, 1 C, exocyclic NCH_2CH_3); isomer **H** (trans−trans), δ 17.22 (s, 4 C, ring NCH_2CH_3), 18.57 (s, 1 C, exocyclic NCH_2CH_3), 39.22 (s, 2 C, exocyclic NCH_2CH_3, isomers **G** and **H**), 39.76 (s, 8 C, ring NCH_2CH_3, isomers **G** and **H**), 115.37, 121.67, 123.10, 124.83, 125.12, 125.42, 125.80, 125.91, 126.57, 129.09, 129.93, 130.12, 131.37, 141.90, 142.23, 152.59 and 152.70 (aryl carbon nuclei for isomers **G** and **H**).

X-ray Structure Determination. Details of the X-ray crystallographic study of **5** are already reported.[3] The crystal data and parameters pertinent to the structure determination of **8** are given in Table 2. A suitable crystal of **8** was coated with paraffin oil, and the intensity data was collected using an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation, at 293 K. The data were corrected for Lorentz, polarization, and absorption[9] effects. The structure was solved by direct methods using SHELXS 86.[10] Full-matrix least-squares refinement was carried out on $|F_o|^2$ using SHELXL 93.[11] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed on the respective atoms in their calculated positions and were allowed to ride on the attached atoms during refinement.

Results and Discussion

Synthesis. The reactions of the λ^3-cyclotriphosphazanes **1**−**3** with TCB yield the λ^5-cyclodiphosphazanes **5**−**7** bearing an

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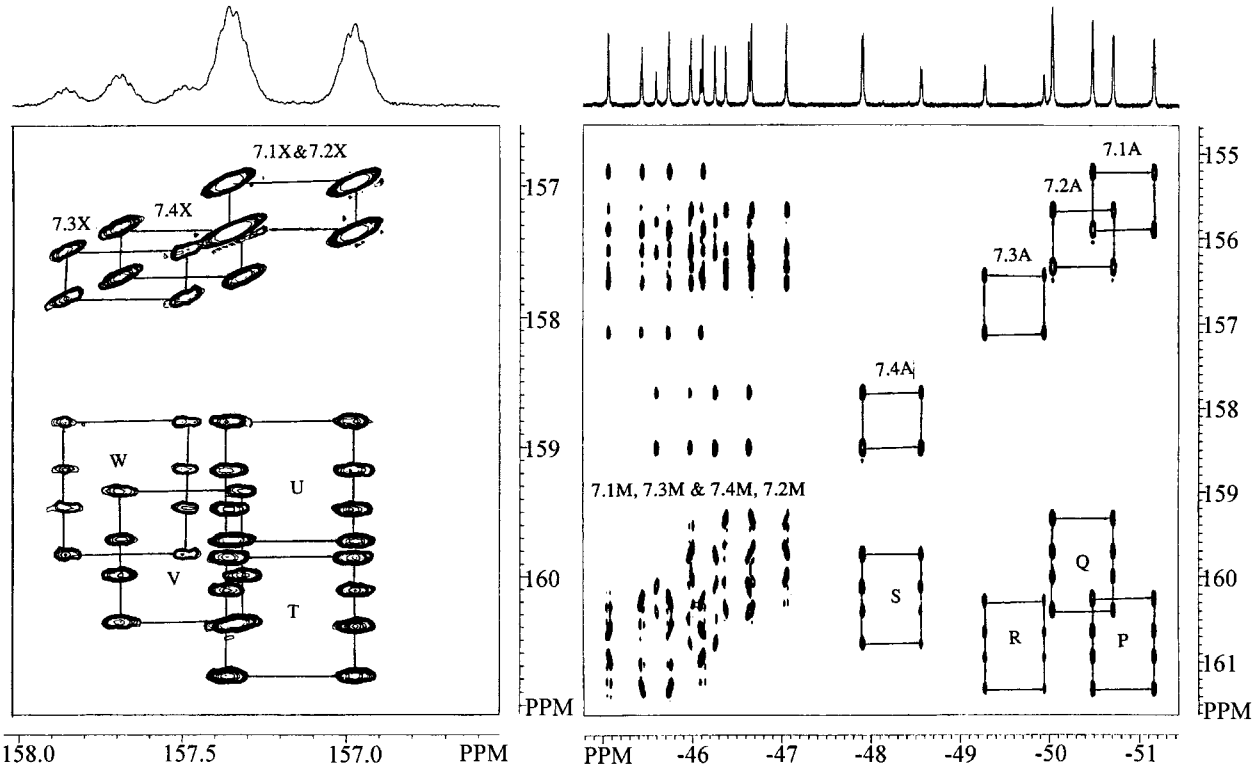


Figure 1. The $^{31}P-^{31}P$ COSY NMR spectrum (243 MHz, CD_2Cl_2) of **7**: (a) X region; (b) A and M regions.

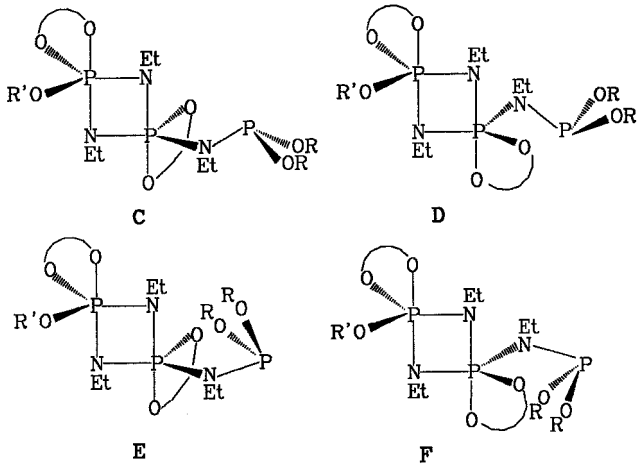


Figure 2. Possible isomers for λ^5-cyclodiphosphazanes [EtNP($O_2C_6Cl_4$)(OR′)][EtNP($O_2C_6Cl_4$){N(Et)P($OR)_2$}] [R = R′ = 2,6-$Me_2C_6H_3$ (**5**), 4-BrC_6H_4 (**6**), CH_2CF_3 (**7**); R = 2,6-$Me_2C_6H_3$, R′ = 4-BrC_6H_4 (**8**).

exocyclic aminophosphite moiety by an unusual ring contraction−rearrangement. One can envisage the formation of an intermediate such as **A** which undergoes subsequent rearrangement although no evidence has been obtained for such an intermediate (Scheme 1). Compounds **5**−**7** are high-melting solids stable to air and moisture. The ease with which the above reaction proceeds depends on the steric bulk of the substituent on the phosphorus atoms. For example, the reaction between **3** and TCB goes to completion in 4 h whereas the reaction of **1** with TCB requires 6 h for completion. Also, the reaction of either cis or trans or a mixture of cis−trans isomers of λ^3-cyclotriphosphazanes **1**−**3** with TCB yields the same product. Treatment of **1** or **2** with other diones such as diacetyl, benzil, or acenaphthenequinone did not give any pentacoordinated products. Evidently, a strong electrophilic dione such as TCB is required to obtain a pentacoordinated phosphorus compound.

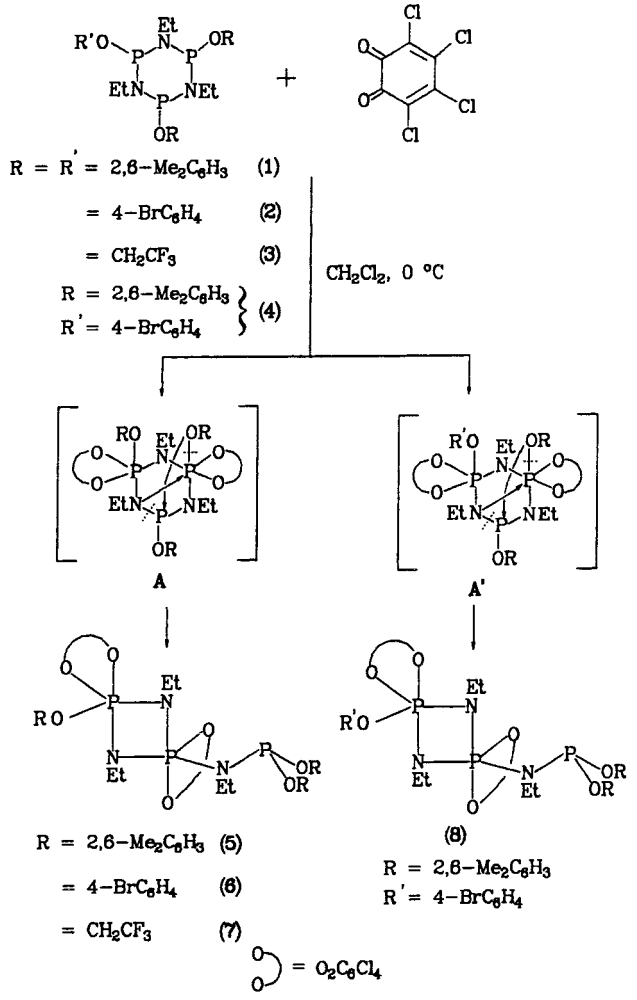
Table 2. Crystallographic Data for **8**

formula	$C_{40}H_{37}BrCl_8N_3O_7P_3$
fw	1128.15
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
cryst size, mm	0.15 × 0.06 × 0.05
a, Å	11.027(1)
b, Å	14.226(4)
c, Å	16.143(2)
α, deg	87.19(2)
β, deg	73.42(1)
γ, deg	80.47(1)
V, Å^3	2393.6(8)
Z	2
ρ_{calcd}, g cm^{-3}	1.565
μ(Mo Kα), cm^{-1}	14.56
λ(Mo Kα), Å	0.7107
scan method	$\omega-2\theta$
2θ range, deg	$2 \le 2\theta \le 50$
τ_{min}, τ_{max}	0.999, 1.131
index range	$0 \le h \le 13$
	$-19 \le k \le 16$
	$-18 \le l \le 19$
reflns	
unique	8390
with $[I > 2\sigma(I)]$	3775
data/restraints/params	8380/0/566
F(000)	1140
residual (negative) peak, e Å^{-3}	0.278 (−0.648)
R1,[a] wR2[b]	0.0777, 0.1360
S[c]	1.127

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

The driving force for the above rearrangement could be the ease with which a pentacoordinated phosphorus atom can be accommodated in a four-membered ring rather than in a six-membered ring and a possible "transannular interaction" of the oxygen atom of an OR group bonded to a pentacoordinated phosphorus atom with the adjacent λ^3-phosphorus center as revealed by the

Scheme 1



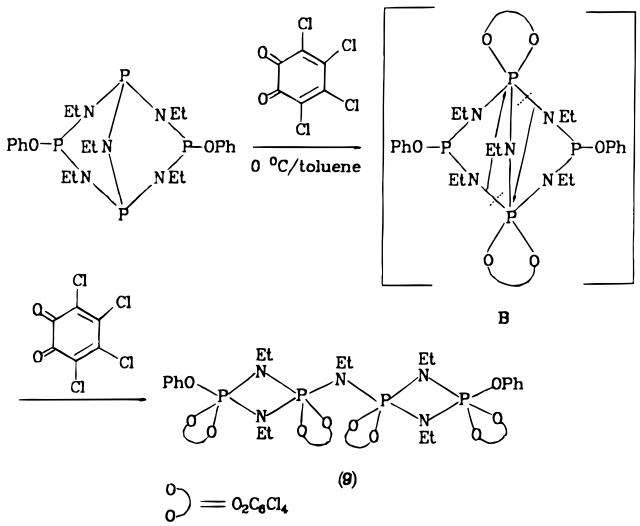
optimized geometries for the model system $[P_3N_3H_3(OH)_3(O_2C_2H_2)_2]$.[3]

To investigate the effect of substituents on the rearrangment reaction, a mixed substituent λ^3-cyclotriphosphazane **4** has been synthesized and isolated as a cis−trans isomeric mixture. Reaction of **4** with TCB yields a rearranged product **8** in which the 4-bromophenoxide resides on one of the ring phosphorus atoms (Scheme 1). If the rearrangment were to proceed via an intermediate of type **A**, then TCB would have initially attacked the phosphorus atom bearing 4-bromophenoxy and 2,6-dimethylphenoxy substituents (structure **A′** in Scheme 1) and not those having 2,6-dimethylphenoxy substituents. It appears likely that steric factors play an important role in the ring-contraction rearrangement reaction.

The λ^3-bicyclic tetraphosphapentazane $(EtN)_5P_4(OPh)_2$ on treatment with TCB gives the λ^5-cyclodiphosphazane **9** presumably via the intermediate **B** by a double ring-contraction rearrangement as depicted in Scheme 2. The proposed mechanism is based on the fact that the bicyclic phosphazane monoxide $(EtN)_5P_4(O)(OPh)_2$ reacts with TCB at the bridging phosphorus to give $[(EtN)_5P_4(O)(O_2C_6Cl_4)(OPh)_2]$.[8]

Spectroscopic Studies. The cyclotriphosphazane **4** has been characterized by ^{31}P NMR and mass spectrometry. The ^{31}P NMR spectrum of **4** gives rise to two sets of signals; the intensity ratio within each set is 2:1. The resonances at 96.7 and 98.2 ppm are assigned to the cis isomer; those at 123.9 and 127.1 ppm arise from the trans isomer. The chemical shifts of the cis

Scheme 2



isomer occur upfield of those of the trans isomer as observed for symmetrically substituted λ^3-cyclotriphosphazanes.[7]

The IR spectra of **5**−**9** show strong bands in the region 800−900 cm^{-1} which can be attributed to ν_{asym}(PNP) vibration of the P_2N_2 ring.[12] Two AMX patterns are found in the ^{31}P NMR spectra of **5**, **6**, and **8**, indicating the presence of two isomers in solution (see Table 1). The A and M nuclei resonate in the pentacoordinated phosphorus region, and the X nucleus resonates in the tricoordinated phosphorus region. The ^{31}P NMR spectrum of **7** recorded at 162 MHz is complex and could not be analyzed because of line broadening (in the X region) and overlapping of resonances in the A and M region. Hence, its ^{31}P−^{31}P COSY NMR spectrum has been recorded at a higher field (243 MHz) and is shown in Figure 1. The first segment (Figure 1a) pertains to the X region and the second segment (Figure 1b) to the A and M region. The contours on the diagonal labeled 7.1A, 7.2A, 7.3A, and 7.4A have four cross peaks designated as P, Q, R, and S, respectively. One can therefore, conclude that the phosphorus nucleus represented by 7.1A (−50.8 ppm, d) is coupled to the phosphorus nucleus corresponding to 7.1M (−45.6 ppm, dd). Similarly, the cross peaks Q, R, and S demonstrate that the phosphorus nuclei represented by 7.2A, 7.3A, and 7.4A (−50.4, −49.6, and −48.2 ppm, d) respectively are coupled to the phosphorus nuclei corresponding to 7.2M, 7.3M, and 7.4M (−46.5, −45.6, and −46.1 ppm, dd). In this way, the entire ^{31}P coupling network can be traced and it clearly shows the presence of four distinct isomers in solution for **7**.

There are four possible isomers for λ^5-cyclodiphosphazanes **5**−**8** as shown in Figure 2. All of these are significantly populated in the case of **7**. The two major isomers are assigned gauche (**C**) and trans (**D**) configurations; the other two minor isomers **E** and **F** arise due to restricted rotation around the exocyclic λ^3-P−N bond. Only two isomers (**C** and **D**) are observed for the cyclodiphosphazanes **5**, **6**, and **8**; in these cases the isomers **E** and **F** are probably excluded because of bulky aryloxy substituents. This observation is also consistent with the broad signals observed in the X region of the ^{31}P NMR spectrum of **7** unlike the sharp signals in the spectra of **5**, **6**, and **8**.

The ^{31}P NMR spectrum of **5** was recorded immediately after the sample was dissolved at 213 K. The spectrum showed the

(12) Keat, R.; Rycroft, D. S.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1980**, 321−326.

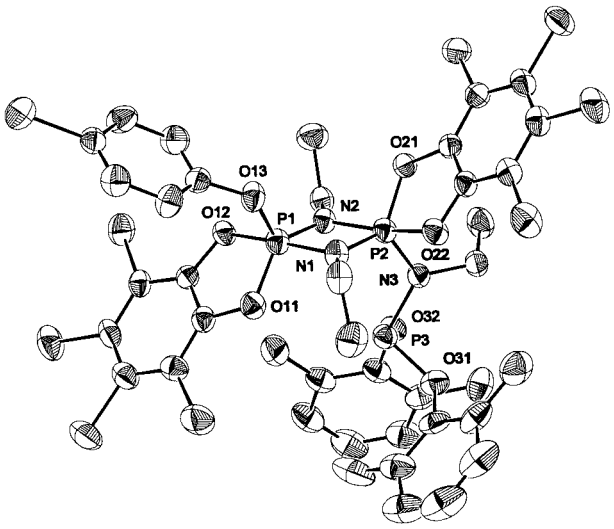


Figure 3. Molecular structure of **8**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(1) 1.712(6), P(1)−N(2) 1.621(6), P(1)−O(11) 1.650(6), P(1)−O(13) 1.600(5), P(1)−O(12) 1.720(5), P(2)−N(1) 1.632(6), P(2)−N(2) 1.747(6), P(2)−N(3) 1.678(6), P(2)−O(21) 1.653(5), P(2)−O(22) 1.740(5), P(3)−N(3) 1.694(6), O(13)−P(1)−N(2) 119.2(3), O(13)−P(1)−O(11) 109.2(3), N(2)−P(1)−O(11) 131.3(3), N(1)−P(1)−O(12) 170.9(3), N(1)−P(2)−O(21) 131.3(3), N(1)−P(2)−N(3) 120.4(3), O(21)−P(2)−N(3) 108.1(3), O(22)−P(2)−N(2) 166.3(3), P(2)−N(3)−P(3) 117.4(3).

presence of two isomers in the ratio 7:1; the population of the minor isomer increased with temperature, and at 25 °C, the ratio of the two isomers was 2:1. Cooling the sample to 213 K did not alter this ratio. These observations suggest that the major isomer in solution has the gauche configuration **C** as observed in the solid state. We tentatively assign gauche configuration **C** to the major isomer of **8** although in this case the trans isomer crystallizes out preferentially.

The ^{1}H and ^{13}C NMR spectra of **5** also reveal the presence of two isomers in solution. Two distinct signals are observed for the ring and exocyclic NCH_2CH_3 protons as well as for the methyl protons of the aryl moiety for each isomer. Furthermore, the ring NCH_2CH_3 protons resonate at a higher field compared to the exocyclic NCH_2CH_3 protons. The ^{13}C NMR spectrum of **5** displays two singlets for the methyl carbon nuclei of the aryl moiety for each isomer presumably owing to the restricted rotation around the λ^3-P−O bond.

The ^{31}P NMR spectrum of **9** shows the presence of two isomers each giving rise to an AB type pattern. The chemical shifts of both A and B nuclei lie in the pentacoordinated phosphorus region. The ^{1}H NMR spectrum shows two sets of triplets [1.14, 1.41 ppm (isomer **G**) and 1.18, 1.23 ppm (isomer **H**)] for the NCH$_2$CH_3 protons in a ratio of ∼1.4:1. Within each set, the intensity ratio is 4:1. The ^{13}C NMR spectrum also displays two sets of signals [16.97, 18.23 ppm (isomer **G**) and 17.22, 18.57 ppm (isomer **H**)] for the NCH$_2$CH_3 carbon nuclei. Tentatively we assign gauche−gauche and trans−trans configurations to the two isomers **G** and **H**, respectively.

Structure of Cyclodiphosphazane 8. The molecular structure of **8** is shown in Figure 3. The structural features of **5** and **8** are compared in Table 3. The P_2N_2 ring in both compounds is planar. The aryloxy substituent on P(1) and the aminophosphite moiety on P(2) are cis to one another in **5** whereas they are trans to each other in **8**. In both the compounds, the aryloxy substituents on P(3) and the ethyl group on N(3) are cis to one another. The conformers **E** and **F** in which these aryloxy substituents are trans to the ethyl group on N(3) would cause severe steric interactions with the substituents on P(2).

Table 3. Comparison of Structural Features of **5** and **8**

salient features	**5**[a]	**8**
conformation of P_2N_2/PO_2C_2 rings	planar/envelope, planar	planar/envelope, envelope
av (P−N)$_{ring}$ distances, Å		
(P−N)$_{apical}$	1.735(2)	1.730(6)
(P−N)$_{equatorial}$	1.637(2)	1.626(6)
av (P−O)$_{exocyclic}$, Å	1.648(2)	1.634(6)
av (PNP)$_{ring}$, deg	99.7(1)	99.9(3)
av (NPN)$_{ring}$, deg	80.3(1)	80.1(3)
Σ(P$_{exocyclic}$) angle, deg	294.9	292.6
range of angle (deg) at		
P(1) (equatorial−equatorial)	109.5−125.2	109.2−131.3
P(1) (apical−equatorial)	80.6−93.9	80.7−94.9
P(2) (equatorial−equatorial)	115.5−125.3	108.1−131.3
P(2) (apical−equatorial)	79.9−98.4	79.4−98.6
dihedral angle φ, deg[b]	48.2, 56.3	45.4, 48.8
dihedral angle φ', deg[c]	52.7	30.1

[a] Data from ref 3. [b] Dihedral angle between the mean plane defined by the five-membered PO_2C_2 and four-membered P_2N_2 rings. [c] Dihedral angle between the mean plane defined by P(3), N(3), C(21), P(2) and that defined by P(2), N(1), O(21), N(3) in **8** [P(3), N(3), C(23), P(2) and P(2), N(2), O(21), N(3) in **5**]. See ref 3 for labeling.

The pentacoordinated phosphorus atoms display a distorted trigonal bipyramidal geometry. The dihedral angle method[13] suggests that the distortion follows a non-Berry coordinate due to ring strain arising from the presence of a four-membered P_2N_2 ring. Each NEt group in the P_2N_2 ring is apical to one phosphorus atom and equatorial to the other. The two oxygen atoms of catecholate moieties span an apical and an equatorial site of a trigonal bipyramid. The geometry around the ring as well as exocyclic nitrogen atoms is planar. The apical bonds are longer than the equatorial bonds. The angle between the apical substituents deviates considerably from an ideal value of 180°. The exocyclic phosphorus atom, P(3), displays a pronounced pyramidal character, and its bond distance to N(3) is longer than the P−N bonds connected to the F_2P or O_2P unit in diphosphinoamines of the type $X_2PN(R)PY_2$.[14] Furthermore, the average λ^3-P−O distances are shorter than those observed in the diphosphinoamine, $Ph_2PN(Pr^i)P(O_2C_6H_4)$ [average (P−O) 1.689(3) Å].[14c] The lengthening of P(3)−N(3) and shortening of λ^3-P−O bonds can be explained by a decreased "negative hyperconjugative" interaction[7] involving lone pairs of electrons on N(3) and P−O σ^* orbitals due to the presence of bulky 2,6-dimethylphenoxy substituents on P(3). If "negative hyperconjugation" is decreased, then one would expect the geometry of N(3) to deviate from planarity. However, this is not observed as N(3) is involved in multiple bonding with P(2). In fact, the P(2)−N(3) distance is shorter than the P(3)−N(3) distance. The bond distances around P(2) are slightly longer than those observed around P(1). For effective multiple bonding between P(2) and N(3), the lone pair of electrons on N(3) should orient parallel to equatorial P−O or P−N bonds.[1f] The dihedral angle (φ') between the least squares mean plane defined by P(3), N(3), C(21), P(2) and that defined by P(2), N(1), O(21), N(3) in **8** is 30°. The corresponding angles in **5** and other related phosphoranes containing a P_2N_2 ring, viz., **10** and **11**, are 52.7°, 87.3°,

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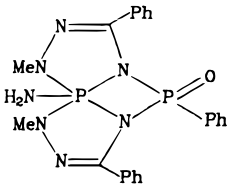
(14) (a) Hedberg, E.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1974**, *96*, 4417−4421. (b) Huntley, C. M.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 954−957. (c) Babu, R. P. K.; Krishnamurthy, S. S.; Nethaji, M. *Heteroat. Chem.* **1991**, *2*, 477−485.

and 61°, respectively.[3,15,16] The observed dihedral angle (φ') of



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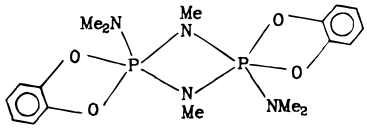

11

30° in **8** indicates that the lone pair of electrons on N(3) is almost parallel to apical bonds. This is presumably due to an unfavorable steric interaction between the substituents on N(3) and apical substituents on P(2). As a result of this orientational effect, apical bond lengths slightly increase while equatorial bond lengths slightly decrease as compared to those observed for **11**.[16] To our knowledge, this is the first structurally characterized phosphorane in which the lone pair on nitrogen lies parallel to apical bonds.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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