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Studies of the Formation and Properties of the Phosphazane Oligomers $[(PhNH)PNPh]_2$ and $[(PhNH)PNPh]_3$

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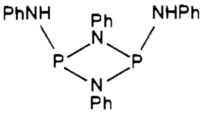
The 1,3,2,4-diazadiphosphetidine-based dimer $[(PhNH)PNPh]_2$ (**1**) or trimer $[(PhNH)PNPh]_3$ (**2**) forms from $(Et_2N)_3P$–$PhNH_2$ transamination or $PhN[P(NHPh)_2]_2$ thermolysis reactions. **2** is an intermediate in the formation of **1** from $PhN[P(NHPh)_2]_2$. An X-ray single-crystal diffraction analysis of the solvate $\mathbf{2}\cdot C_2H_5OH$ has been carried out. $\mathbf{2}\cdot C_2H_5OH$ is monoclinic, space group $C2/c$, with $a = 23.156$ (9) Å, $b = 14.533$ (5) Å, $c = 22.243$ (8) Å, $\beta = 110.63$ (3)°, $Z = 8$, $d_{calcd} = 1.24$ g/cm³, and $d_{obsd} = 1.15$ g/cm³ (24 °C, Mo Kα). $\mathbf{2}\cdot C_2H_5OH$ refined to $R = 0.069$ and $R_w = 0.083$ for 1850 independent reflections. **2** contains PhNH– and $-N(Ph)P(NHPh)_2$ substituents at phosphorus atoms of the 1,3,2,4-diazadiphosphetidine ring. **2** has approximate C_s molecular symmetry. Complete characterization data for **1** are given. The ^{31}P NMR spectrum of **1**, in contrast to that of **2**, is temperature dependent. Below −40 °C, **1** in toluene assumes an unsymmetrical conformation of approximate C_s symmetry in which the PhNH groups are rotated opposite to each other, with respect to the lone-pair electrons of the P_2N_2 ring phosphorus atoms. The dimer (**1**)–trimer (**2**) interconversion is discussed and related to more general phosphazane oligomerization.

Introduction

The 1,3,2,4-diazadiphosphetidine[2] dimer $[(PhNH)PNPh]_2$ (**1**) and trimer $[(PhNH)PNPh]_3$ (**2**)[3,4] oligomers along with the dinuclear $[(PhNH)P_2(NPh)_2]_2NPh$ (**3**),[4,5] form in reactions of PCl_3 with $PhNH_2$ under controlled conditions. Compound **3**, the final reaction product, can be obtained pure and in high yield, whereas **1** and **2** because they are closely related oligomer members and reaction intermediates are more difficult to isolate. However, since **1** and **2** are rare examples of phosphorus(III) phosphazane dimer and trimer oligomer members of type $(XPNR)_n$, it is especially interesting to obtain them easily and to study them further.



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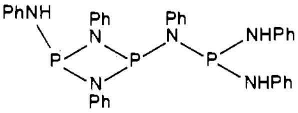

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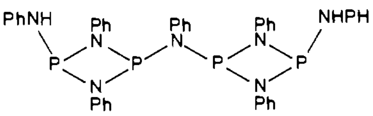

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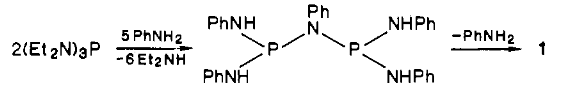
Earlier we reported that the $(Et_2N)_3P$–$PhNH_2$ transamination reaction yields stepwise the triaminophosphine $(PhNH)_3P$ and the diphosphazane $PhN[P(NHPh)_2]_2$ (**4**) en route to dimer **1** (eq 1),[6] in a reaction more complex than recognized previously.[7] In addition **1** had been incompletely characterized, leaving the nature of the final product(s) of the $(Et_2N)_3P$–$PhNH_2$ transamination reaction unclear. Since **1** is the $n = 2$ member of the $[(PhNH)PNPh]_n$ oligomer series, it seemed possible that under some conditions **2** or a mixture of **2** and **1** could be the product of the reaction. Consequently, we have further examined the $(Et_2N)_3P$–$PhNH_2$ reaction system and studied the properties of **1** and **2** in detail. The results of these studies are reported below.



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Experimental Section

Apparatus and Materials. All manipulations were carried out under N_2.[8] ^1H NMR spectra were obtained at 90.0 and 250 MHz with JEOL FX-90Q and Bruker WM250 spectrometers. ^{31}P NMR spectra were obtained at 36.4 and 101.3 MHz with the JEOL FX-90Q and Bruker WM250 spectrometers. ^{31}P and ^1H chemical shifts were measured relative to internal H_3PO_4 and $(CH_3)_4Si$, respectively; $+\delta$ values are downfield from the standards. Mass spectra were obtained by using a Varian MAT CH-5 spectrometer. $(Et_2N)_3P$[9] and $PhN[P(NHPh)_2]_2$[6] were obtained by reported methods. Et_2O (Baker, anhydrous) was used as obtained. Benzene and toluene were distilled from Na/K alloy. Chloroform, CS_2, and CH_2Cl_2 were distilled from P_4O_{10}.

$(Et_2N)_3P + PhNH_2$. (A) $[(PhNH)PNPh]_3$ (2). $(Et_2N)_3P$ (1.4 mmol) and $PhNH_2$ (1.8 mmol) were heated at 80 °C under conditions where Et_2NH could be removed periodically in vacuo. After 2 h, excess $(Et_2N)_3P$ was removed in vacuo. Recrystallization of reaction materials from Et_2O yielded **2** (mp 180–181 °C). $^{31}P\{^1H\}$ NMR (toluene-d_8): 80 to −90 °C, AMX[10] pattern (Figure 1); 24 °C, δ 109.6 [d of d, area 1, $J_{P(2)P(3)} = 12.2$ Hz, $J_{P(1)P(2)} = 359$ Hz, P(2)], δ 106.9 [d, area 1, P(1)], and δ 62.0 [d, area 1, P(3)]; 80 °C, $J_{P(1)P(2)} = 354$ Hz, $J_{P(2)P(3)} = 12.4$ Hz; −90 °C $J_{P(1)P(2)} = 352$ Hz, $J_{P(2)P(3)} = 11.7$ Hz; with ^1H coupling (Figure 1A) the δ 106.9 and 62.0 resonances broaden slightly. **2** crystallizes from a 95:5 (m/m) CH_2Cl_2:C_2H_5OH solution as a monosolvate (see X-ray analysis). IR, mass, and ambient-temperature NMR spectra (^{31}P and ^1H) were reported previously.[5]

In a separate experiment, $PhN[P(NHPh)_2]_2$ in toluene was heated at 100–110 °C (Figure 2A–C). After 3 h, $PhNH_2$ and toluene were removed in vacuo. Recrystallization from Et_2O yielded **1** (80–85% yield).

(B) $[(PhNH)PNPh]_2$ (1). $PhNH_2$ (0.20 mol) and $(Et_2N)_3P$ (0.60 mol) were heated at 55–60 °C for 10 h, periodically removing Et_2NH in vacuo. Toluene was added and the solution heated to reflux. After 3 h, volatile reaction materials were removed in vacuo. Recrystallization of reaction solid from Et_2O yielded pure $\mathbf{1}\cdot Et_2O$ (mp 149–150 °C). Et_2O could be removed in vacuo. Anal. Calcd for $C_{24}H_{22}N_4P_2$: C, 67.29; H, 5.18; N, 13.08; P, 14.46. Found: C, 67.39; H, 5.24; N, 13.50; P, 14.22. IR (KBr pellet), cm^{-1}: 3289 (m), 3155 (w), 2994 (w), 1587 (s), 1479 (vs), 1418 (w), 1362 (m), 1340 (w), 1266 (vs), 1219 (m), 1179 (m), 1075 (m), 1031 (m), 1000 (m), 962 (w), 909 (vs), 881 (vs), 791 (s), 749 (vs), 692 (vs), 662 (m), 619 (w), 550 (m), 500 (s), 474 (w). MS, parent and four most intense envelopes (relative intensity) at m/e 428 (1; M^+), 336 (2), 214 (1), 122 (5), 94 (100). ^1H NMR (toluene-d_8); δ 6.98–6.49 (m, area 20, C_6H_5), 4.51 (d, area 2, $^2J_{PNH} = 12.3$ Hz, NH). ^{31}P NMR (101.3 MHz, toluene, Figure 3A–C): 0 °C, δ 104.6 (s); −85 °C, δ 102.87

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(2) The 1,3,2,4-diazadiphosphetidine nomenclature system advocated by Chemical Abstracts is used throughout this paper. An alternate system, based on the stem name cyclodiphosph(III)azane is frequently used in the European literature.

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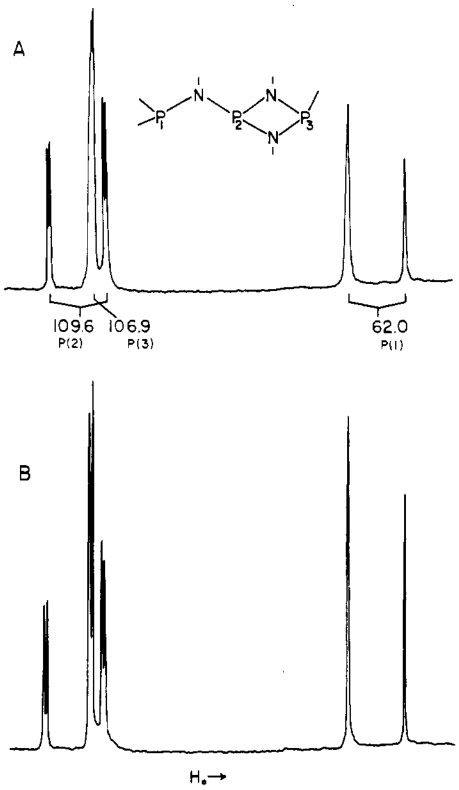


Figure 1. ^{31}P NMR spectra of [(PhNH)PNPh]$_3$ (**2**): (A) ^1H coupled; (B) ^1H decoupled.

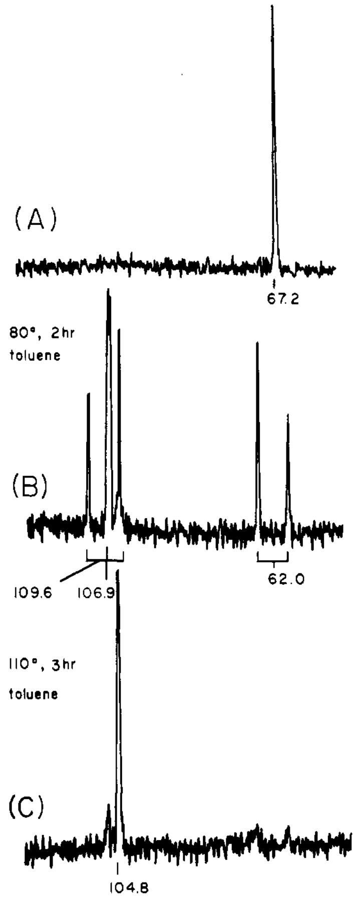


Figure 2. ^{31}P NMR spectra for the conversion of PhN[P(NHPh)$_2$]$_2$ to **1** and **2**: (A) spectrum of the initial PhN[P(NHPh)$_2$]$_2$; (B) spectrum after 2 h at 80 °C; (C) spectrum after 3 h at 110 °C.

[d, area 1, $^2J_{PNP}$ = 9.0 Hz, P(1)] and 101.60 [d of d, area 1, $^2J_{PNP}$ = 9.0 Hz, $^2J_{PNH}$ = 38.4 Hz, P(2)]; t_c = −10 °C.

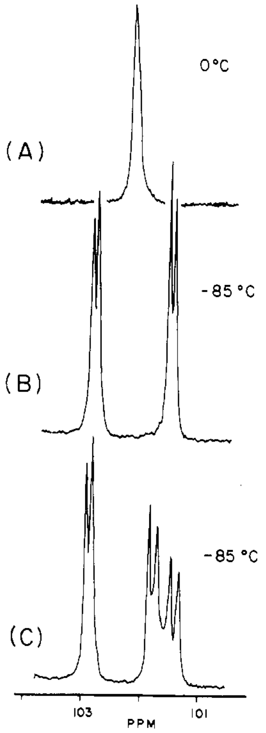


Figure 3. ^{31}P NMR spectra of [(PhNH)PNPh]$_2$ (**1**) at 0 °C (A) and −85 °C (B), ^1H decoupled, and at −85 °C (C), ^1H coupled.

Table I. Crystallographic Data and Data Collection Parameters for [(PhNH)PNPh]$_3$·C_2H_5OH (**2**·EtOH)

formula	$P_3N_6C_{38}H_{39}O$
fw,	688.705
space group	C2/c
a, Å	23.156 (9)[a]
b, Å	14.533 (5)
c, Å	22.243 (8)
β, deg	100.630
V, Å^3	7357 (5)
d_c, g/cm^3	1.24
d_0, g/cm^3	1.15
Z	8
cryst size, mm	0.35 × 0.3 × 0.6
cryst habit	colorless needles
temp, K	297 ± 3
scan mode	θ–2θ
scan speed, deg min^{-1}	2.0–24.0
scan range, deg	1.0 below Kα_1 to 1.0 above Kα_2
2θ limit, deg	3.0–40.0
bkgd time/scan time	0.5
data points	
measd	3568
obsd [$F_o^2 > 3.0(F_o^2)$]	1850
abs cor	none
ratio of observns to params	10:1
R	0.069
R_w	0.083

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

1 is soluble in CH_2Cl_2, $CHCl_3$, C_6H_6, and toluene and moderately soluble in Et_2O. **1** shows no decomposition during 4 days under N_2 at 25 °C but oxidizes slowly in ambient air.

1–2 Solution Equilibration Studies. Samples of **1** or **2** from [(PhNH)$_2$P]$_2$NPh thermolysis or $PhNH_2$–PCl_3[4,5] reactions in NMR tubes (typically 10% in toluene) were heated to constant temperatures of 80–110 °C for 2–6 h to examine sample equilibration. Final **1**:**2** product ratios of 8.5–10:1 were determined from ^{31}P NMR spectral integration.

X-ray Analysis of 2·C_2H_5OH. Crystals of **2**·C_2H_5OH were mounted on a glass fiber and coated with epoxy resin. Cell parameters were determined on the diffractometer and refined by least-squares fit of the parameters to 15 centered reflections. Crystal data and data collection details are given in Table I. Background measurements, collected by

Table II. Atomic Parameters for the Nongroup Atoms of $[(PhNH)PNPh]_3{\cdot}C_2H_5OH$ (**2**·EtOH)

atom	x	y	z	B_{eq},[a] Å^2
P(1)	0.7256 (1)	0.1346 (2)	0.6194 (1)	5.0
P(2)	0.7104 (1)	−0.0285 (2)	0.6891 (1)	5.4
P(3)	0.6804 (2)	−0.2035 (5)	0.6886 (1)	6.1
N(1)	0.7810 (3)	0.1432 (5)	0.5802 (3)	5.4
N(2)	0.6752 (3)	0.1740 (5)	0.5602 (3)	5.3
N(3)	0.7113 (3)	0.0181 (5)	0.6195 (3)	4.4
N(4)	0.7418 (3)	0.1355 (5)	0.6888 (3)	5.5
N(5)	0.6490 (3)	−0.0966 (5)	0.6794 (3)	5.2
N(6)	0.6688 (4)	−0.2495 (5)	0.6184 (3)	6.1
O(1)	0.7294 (5)	0.1480 (6)	0.4489 (4)	8.9
C(1A)	0.7529 (13)	0.0887 (20)	0.4021 (15)	9.0
C(1B)	0.7015 (25)	0.0932 (27)	0.3981 (17)	7.0
C(2)	0.7130 (16)	0.0883 (17)	0.3522 (8)	15.0

[a] $B_{eq} = (B_{11}B_{22}B_{33})^{1/3}$.

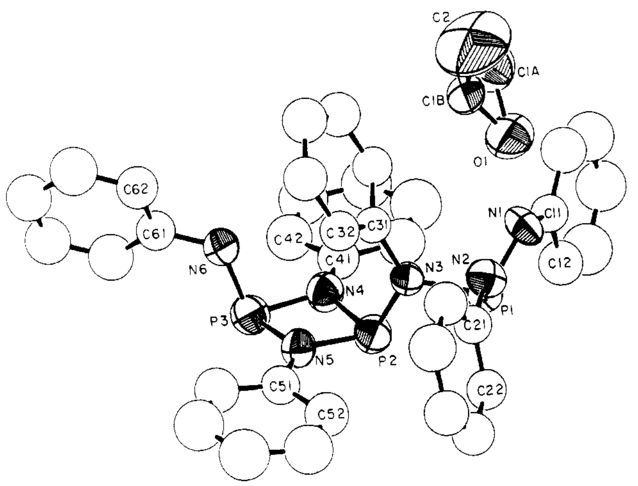


Figure 4. Structure of $[(PhNH)PNPh]_3$ (**2**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity.

Table III. Structural Parameters for $[(PhNH)PNPh]_3{\cdot}C_2H_5OH$ (**2**·EtOH)

(a) Bond Distances (Å)			
P(1)–N(1)	1.682 (7)	O(1)–(C1B)	1.44 (4)
P(1)–N(2)	1.690 (8)	C(2)–(C1A)	1.30 (3)
P(1)–N(3)	1.727 (7)	C(2)–(C1B)	1.10 (3)
P(2)–N(3)	1.694 (7)	C(11)–N(1)	1.412 (9)
P(2)–N(4)	1.720 (8)	C(21)–N(2)	1.395 (10)
P(2)–N(5)	1.7212 (8)	C(31)–N(3)	1.422 (9)
P(3)–N(4)	1.732 (8)	C(41)–N(4)	1.381 (10)
P(3)–N(5)	1.714 (8)	C(51)–N(5)	1.406 (10)
P(3)–N(6)	1.675 (8)	C(61)–N(6)	1.419 (10)
O(1)–(C1A)	1.53 (3)		
(b) Bond Angles (deg)			
N(1)–P(1)–N(2)	93.2 (4)	C(31)–N(3)–P(1)	122.1 (5)
N(1)–P(1)–N(3)	103.8 (4)	P(2)–N(3)–P(2)	115.5 (4)
N(2)–P(1)–N(3)	103.3 (4)	C(41)–N(4)–P(2)	131.8 (6)
N(3)–P(2)–N(4)	106.4 (4)	C(41)–N(4)–P(3)	127.7 (6)
N(3)–P(2)–N(5)	105.5 (4)	P(2)–N(4)–P(3)	99.7 (4)
N(4)–P(2)–N(5)	79.5 (4)	C(51)–N(5)–P(2)	130.5 (6)
N(4)–P(3)–N(5)	79.1 (4)	C(51)–N(5)–P(3)	128.0 (6)
N(4)–P(3)–N(6)	102.8 (4)	P(2)–N(5)–P(3)	100.7 (4)
N(5)–P(3)–N(6)	105.1 (4)	C(61)–N(6)–P(3)	124.2 (6)
C(11)–N(1)–P(1)	123.4 (6)	C(2)–C(1A)–O(1)	107 (3)
C(21)–N(2)–P(1)	123.0 (6)	C(2)–C(1B)–O(1)	128 (4)
C(31)–N(3)–P(2)	122.3 (5)		

using the stationary-crystal–stationary-counter technique were made at the beginning and end of each scan. The standards, monitored every 100 measurement cycles, showed no significant variation over the course of the collection of data for a unique quadrant. Multiple solutions direct methods revealed the position of 39 of the 48 atoms. The remaining atoms, except for the hydrogen atoms associated with the C_2H_5OH solvate, were located by using Fourier techniques. The C_2H_5OH molecule is disordered. The model refined to the values given in Table I with all phenyl groups treated as rigid groups, with individual thermal parameters for each carbon atom, all nongroup atoms treated anisotropically, and hydrogen atoms included in idealized positions with isotropic thermal parameters. The hydrogen atoms associated with the C_2H_5OH were not included. Scattering factors used were for neutral atoms.[11] All calculations were carried out on the University of Colorado's dual CDC 6400 computer using programs contained in or based on Ibers Northwestern Crystallographic Computing Package, the MULTAN 78 package, and Syntex's data reduction routines. Final positional parameters for **2**·C_2H_5OH are given in Table II. Thermal and group parameters are given in the supplementary material.

Results and Discussion

Reaction of $(Et_2N)_3P$ with $PhNH_2$ results in elimination of Et_2NH and formation of either the trimer $[(PhNH)PNPh]_3$ (**2**)

$$6PhNH_2 + 3(Et_2N)_3P \rightarrow 9Et_2NH + \underset{\mathbf{2}}{[(PhNH)PNPh]_3} \quad (2)$$

or dimer $[(PhNH)PNPh]_2$ (**1**)

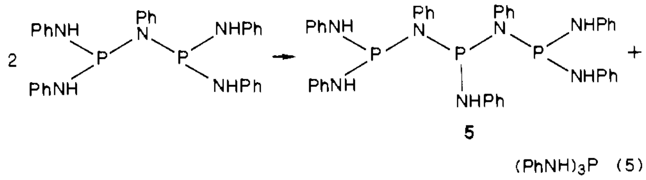
$$4PhNH_2 + 2(Et_2N)_3P \rightarrow 6Et_2NH + \underset{\mathbf{1}}{[(PhNH)PNPh]_2} \quad (3)$$

in high yield depending on reaction conditions. Trimer (**2**) can be obtained from reaction at 80 °C, whereas at higher temperatures (e.g. 110 °C), **1** is formed. In both situations, the product is formed almost quantitatively. Similarly, thermolysis of $[(PhNH)_2P]_2NPh$ (Figure 2A) at 80 °C yields **2** initially

$$3[(PhNH)_2P]_2NPh \rightarrow 3PhNH_2 + 2[(PhNH)PNPh]_3 \quad (4)$$

(Figure 2B) and later **1** at 110 °C (Figure 2C), in a reaction that from ^{31}P NMR spectral analysis is surprisingly clean. Only **3** forms slowly at 110 °C. For either **1** or **2**, the $(Et_2N)_3P$–$PhNH_2$ or $PhN[P(NHPh)_2]_2$ thermolyses constitute excellent syntheses, superior to the PCl_3–$PhNH_2$ reaction,[3] largely because no $PhNH_3Cl$ is present, which makes purification difficult.

The sequence of product formation in the $(Et_2N)_3P$–$PhNH_2$ reaction is $(Et_2N)_2PNHPh$, $Et_2NP(NHPh)_2$, $(PhNH)_3P$, $PhN[P(NHPh)_2]_2$, **2**, and finally **1**. Formation of the first four products had been established previously.[6] For the three-phosphorus phosphazane **2** to precede the two-phosphorus product **1** in the sequence is unusual. Examination of ^{31}P NMR spectra taken sequentially shows no evidence for other species; however, a process such as that in eq 5, in which two molecules of $PhN[P(NHPh)_2]_2$



(5)

react to eliminate $(PhNH)_3P$ and form acyclic intermediate **5** can be considered. Elimination of $PhNH_2$ from **5** accompanied by ring closure would produce **2**. The $(PhNH)_3P$ would be converted rapidly back to $PhN[P(NHPh)_2]_2$[6].

Trimer **2** has been characterized previously on the basis of spectral data,[5] as a 1,3,2,4-diazadiphosphetidine-based phosphazane. This structure has been confirmed now by an X-ray structural study in which details of structure, especially conformation, can be established. X-ray analysis was performed on the C_2H_5OH monosolvate, **2**·C_2H_5OH. The structure of **2** along with the numbering scheme used is shown in Figure 4. The unit cell contains eight molecules. Intramolecular bond distances and angles are listed in Table III. **2** contains a P_2N_2 ring to which PhNH– and $(PhNH)_2PN(Ph)$– groups are cis bonded at P(2) and P(3), giving the molecule pseudo-C_s molecular symmetry. The central N atoms of the PhNH– and $(PhNH)_2PN(Ph)$– units are trigonal planar, oriented such that the trigonal plane is parallel with the P···P axis of the P_2N_2 ring. Structural parameters of **2** are closely similar, insofar as they can be compared, to the dinuclear **3** and other amino-substituted P(III) 1,3,2,4-diazadiphosphetidines.[3,12-18] Mean P–N ring distances in **2** (1.720 Å)

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[11] Ibers, J. A.; Hamilton, W. C., Eds. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

are within the range 1.68–1.72 Å observed previously.

The P_2N_2 ring of **2** is nearly planar, bent slightly along the N···N axis such that the substituents on phosphorus are tilted away from each other. The interplane dihedral angle between planes P(2),N(4),N(5) and P(3),N(4),N(5) in **2** is 9.1°, comparable to the angle of 11.2° in **3** but smaller than observed in alkylamino-substituted *cis*-1,3,2,4-diazadiphosphetidines.[12-17] These are in contrast to the arylamino-substituted *cis*-$(PClNPh)_2$, which is planar.[12] Possibly, weak π-bonding interactions between the P_2N_2 ring and *N*-aryl groups[12,19,20] are not large enough to overcome the steric repulsions[21] between the substituent groups in **2**.

Compound **2** assumes conformations around bond units in the molecules closely similar to those in **3**, $PhN[P(NHPh)_2]_2$,[6] and $PhN(PCl_2)_2$.[22] In **2**, like **5**, the P_2N_2 ring *N*-aryl groups approach coplanarity with the P_2N_2 planes. **2**, **3**[5] and $PhN[P(NHPh)_2]_2$[6] assume conformations around central P–N–P bonds that essentially eclipse phosphorus lone-pair electrons. The dihedral angle between perpendiculars to the N(3),N(4),N(5) and N(1),N(2),N(3) planes in **2** is 10.1°. Thus, it can be expected that **2**, like **3** and $PhN[P(NHPh)_2]_2$, might have interesting coordination chemistry.

Dimer **1** can now be unambiguously characterized by spectral (IR, MS, and ^{31}P and ^1H NMR) data and its structure established by comparison of these data to those for **2** and **3**. The mass spectrum of **1** shows a parent ion at *m/e* 428, clearly distinct from that of **2** or the higher molecular weight dinuclear **3**. The ^1H NMR spectrum exhibits resonances at δ 6.98–6.49 and 4.51 in an area ratio of 20:2, attributable to the Ph and NH protons, respectively. Comparison of the ^{31}P NMR chemical shift of **1** (δ 104.9), with shifts of the ring phosphorus atoms in the closely related **2** (δ 109.6 and 106.9),[3-5] *trans*-$[(Ph_2N)PNPh]_2$,[12] or the alkyl-substituted compounds *cis*- and *trans*-$(R_2NPNR')_2$ (R and R′ = alkyl),[13] shows that **1** is the cis isomer. No resonances at lower field δ 160–190, in the region characteristic of trans isomers are seen.[3,4,6,13-20] From the $(Et_2N)_3P–PhNH_2$ or $PhN[P(NHPh)_2]_2$ reactions, just as from the $PhNH_2–PCl_3$ reaction, **1** is apparently either formed only as the cis isomer or rapidly converted to the cis isomer after formation. Thus we conclude that for **1**, **2**, and **3**, the cis isomers are thermodynamically preferred.

The conformational properties of the P_2N_2 ring exo-group substituents in **1**, **2**, and **3** in solution are of interest to compare. They can be inferred from ^{31}P NMR spectral data. The ^{31}P NMR spectra of **2** in toluene as a function of temperature over the range +80 to −90 °C shows only the AMX[10] characteristic resonance pattern at δ 109.6, 106.9, and 62.0 assigned to phosphorus atoms P(2), P(3), and P(1), respectively (Figure 1B). Except for a small chemical shift dependence, the spectrum is temperature independent. Above 80 °C, **2** converts rapidly to **1**. A similar lack of temperature dependence has been noted for the dinuclear compound **3**.[5] With ^1H coupling, the spectrum of **2** is unchanged except for slight broadening of the P(2) and P(1) resonances at δ 106.9 and 62.0 (Figure 1A). In contrast, the spectrum of **1** is markedly temperature dependent. Between 80 and 0 °C in toluene (Figure 3A), the $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance. As the temperature is lowered, the singlet broadens until at −30 °C clear separation into two equal-area peaks occurs. At −85 °C, two coupled ($^2J_{PP}$ = 11.7 Hz) doublets at δ 101.60 and 102.87 appear. Upon ^1H coupling (Figure 3C), the δ 102.87 member broadens slightly and the higher field resonance splits into a doublet ($^2J_{PNH}$ = 38.4 Hz).

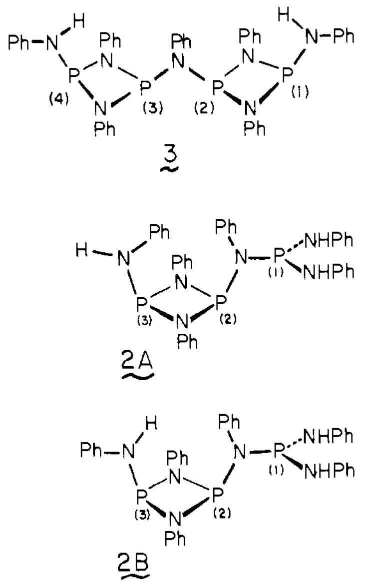

Figure 5. Structure of **2** and **3**. The conformation of **3** is that observed in the solid; **2A** and **2B** are limiting conformations for $[(PhNH)PNPh]_3$ (**2**) (**2B** observed in the solid).

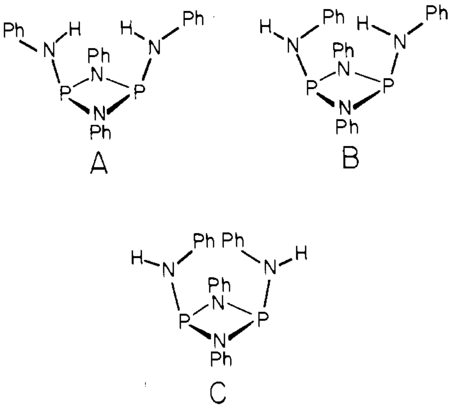

Figure 6. Limiting conformations for $[(PhNH)PNPh]_2$ (**1**).

The ^{31}P NMR spectrum of **1** at −85 °C suggests the presence of one unsymmetrical conformer, a conformer that results from the unsymmetrical "freezing" of PhNH units around the exo P–N bonds. One PhNH group is weakly coupled ($^2J_{PNH} < 5$ Hz) and the other strongly coupled (J_{PNH} = 38.4 Hz) to its bonded phosphorus atom. In contrast, **2** and **3** show only one spectral pattern over the entire temperature range, consistent with them being retained in one conformation. The X-ray structures of **2** and **3** show they both assume conformations in the solid in which the exo PhNH group is rotated around the P–N bond such that the N–H bond is trans to the phosphorus lone-pair electrons (**3** and **2B**, Figure 5). In these, the exo nitrogen atoms are planar with their lone-pair electrons in a p_z orbital perpendicular to the phosphorus atom lone-pair electrons. Assuming the lowest energy conformations for **2** and **3** in the solid are the same as in solution, the ^{31}P NMR spectral data can be correlated with structure; i.e., it is the trans conformation (**2B**, Figure 5), that has the small $^2J_{PNH}$ coupling constant. Thus in **1** at −85 °C, the 12-Hz coupling ($^2J_{PNH}$) appears due to a trans-rotated PhNH group. The larger $^2J_{PNH}$ coupling is due to a cis oriented PhNH group, as in conformation B, Figure 6. That the J_{PNH} coupling in differently

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oriented exo RR′N groups is a function of orientation is not unexpected. In dialkylamino-substituted diazadiphosphetidines a similar situation with respect to $^2J_{PNC}$ and $^3J_{PNCH}$ couplings occurs, although the unambiguous correlation of coupling constants with structure based on X-ray crystallographic data was not accomplished.[23]

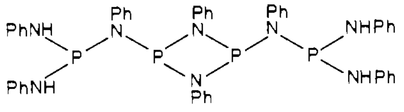
The coalescence temperature for bond rotation is −10 °C. From the equation $\Delta G^{\ddagger}_{T_c} = T_c\,[45.63 + 4.58 \log (T_c/\Delta\nu)]$ cal/mol (T_c = coalescence temperature, ΔV = shift in Hz in absence of exchange),[24,25] a $\Delta G^{\ddagger}_T$ value of 12.4 ± 0.3 kcal/mol for **1** in toluene is determined. This barrier to P–N bond rotation is comparable to P–N rotation barriers measured previously,[16,26–29] lower than the barrier of 17.6 kcal/mol reported for rotation around exo Me_2N–P bonds in $[(Me_2N)PN(t\text{-}Bu)]_2$[16] but similar to the barrier of 12.6 kcal/mol observed in *N*-aryl ring-substituted $[(Me_2N)PNPh]_2$.[16]

Why conformation B (Figure 6) for **1** is more stable than A is not clear since orientation of a Ph ring over the P_2N_2 ring seems sterically unfavorable. However, this situation is seen elsewhere in cases where the RR′N groups are unsymmetrical and a choice in orientation exists; e.g., in *trans*-[(PhNH)P(S)NPh]$_2$,[30] *trans*-[Ph(Me)NP(S)NPh]$_2$,[31] and *trans*-[Ph(Et)NP(S)NPh]$_2$,[31] the phenyl groups locate over the P_2N_2 rings. The RR′N exo group orientation may be the result of balancing the intramolecular RR′N exo–exo interactions versus RR′N(exo)–R″(endo) interactions. Keat argues[16] that such conformational effects cause the lone-pair electrons of the N atom of the RR′N groups and the ring phosphorus atoms to be orthogonal. Perhaps, given that the exo groups are parallel to the P_2N_2 P···P vector, the R group repulsions in **1** are minimized by one Ph group being in and one being out. These conformational effects seem unique and deserve further study.

Compounds **1** and **2** are middle members of the oligomeric series $[(PhNH)PNPh]_n$ based on diazadiphosphetidine rings. Monomer (n = 1; **7**) and tetramer (n = 4; **8**) members were not observed

$PhNHP{=}NPh$

7



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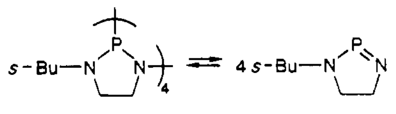
although their possible existence is interesting to speculate upon. **1** and **2** are stable for long periods in solution at ambient temperatures. However, at higher temperatures, **1** or **2** react to establish a **1**–**2** equilibrium mixture according to

$$2[(PhNH)PNPh]_3 \rightleftarrows 3[(PhNH)PNPh]_2 \qquad (6)$$

When either **1** or **2** is heated, while reaction progress is monitored by ^{31}P NMR spectral analysis, reaction yields resonances due to both **1** and **2**. No resonances attributable to either monomer or tetramer were seen, although the equilibration reaction is accompanied by a slower side reaction that produces **3**. In addition, reactions appear sensitive to traces of catalysts/impurities that affect the rate of approach to equilibrium and complicate quantitative measurements. These make measurement of reliable equilibrium constants difficult; however, **1**:**2** ratios of 8:5–10:1 were observed. It appears clear that dimer (**1**) is favored at equilibrium at 100 °C. Further studies to elucidate the role of catalysts in the equilibration process are in progress.

The **1**–**2** interconversion reaction is an example of a rare interconversion between P(III) phosphazane oligomer members.[32,33] Monomers of general formula $R_2NP{=}NR$ are known to dimerize, generally irreversibly, to dimers $(R_2NPNR)_2$.[34] In one instance,[32c] Malavaud has shown that equilibrium exists between the cyclic tetramer **9** and the phosphazene monomer **10**. The **9**:**10** ratio



(7)

9 10

at equilibrium ranges from 100:0 at 60 °C to 0:100 at 150 °C. It is interesting that at higher temperatures the lower oligomer member, **10** (n = 1), is favored. Although we have been able to measure the equilibrium between **1** and **2** only qualitatively and over a narrow temperature range, **1** is favored at high temperature. This is expected, on the basis of entropy considerations, and also is as observed in the phosphazene $(PX_2N)_n$ series.[35,36]

It is not clear why the $[(PhNH)NPh]_3$ trimer is diazadiphosphetidine ring based instead of six-membered ring based as is observed for the $[(PX)NR]_3$ (X = Cl, Br; R = Me, Et) species.[13,16,37] In the $[(PhNH)PNPh]_x$ system, the P_2N_2 rings are preferred. No evidence for six-membered ring species is seen in the ^{31}P NMR spectrum of **1**, **2**, or **1**–**2** mixtures. Possibly the Ph and PhNH groups are large enough to make larger ring formation prohibitive.[16] It is of interest to see if with other larger R groups, analogous diazadiphosphetidine-based $[(PX)NR]_3$ molecules can be prepared.

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Supplementary Material Available: Tables of nongroup atom anisotropic thermal parameters, rigid-group derived parameters, idealized hydrogen atom positions, and least-squares planes, deviations from planes, and interplane angles for **2**·C_2H_5OH (6 pages); a table of structure factors for **2**·C_2H_5OH (6 pages). Ordering information is given on any current masthead page.

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