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Gallium Halide Induced Heterocycle Expansion of Dihalodiphosphadiaryldiazanes [$(XPNR)_2$] to the Corresponding Triphosphatriazanes [$(XPNR)_3$]

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Reactions of the cyclic diphosphadiazanes $(XPNR)_2$ (X = Cl, Br; R = 2,6-dimethylphenyl = Dmp, 2,6-diisopropylphenyl = Dipp) with GaX_3 followed by 4-(dimethylamino)pyridine (DMAP) give the corresponding trimers $(XPNR)_3$. An unusual cyclophosphazanium tetrachlorogallate salt $[(DippN)_3P_3Cl_2][GaCl_4]$ has been isolated from the reaction of $(ClPNDipp)_2$ with $GaCl_3$ and represents an intermediate in the disproportionation process. Dissociation of the gallate ion on reaction of $[(DippN)_3P_3Cl_2][GaCl_4]$ with DMAP releases a halide ion, which associates with the dicoordinate phosphenium center to give $(ClPNDipp)_3$. The observations indicate that the presence of medium-sized substituents at nitrogen (R) thermodynamically destabilize the dimer with respect to the trimer, without offering sufficient stabilization of the monomer, as observed for Mes*NPX (Mes* = 2,4,6-tri-*tert*-butylphenyl) (Mes* > Dipp > Dmp). Nevertheless, lability of the N–P bond in these derivatives of $(XPNR)_2$ allows for transformations between dimer and trimer that may include transient existence of the corresponding monomer. Manipulation of substituent steric strain to modify the relative stability of phosphazane oligomers provides a new methodology for diversification of phosphazane chemistry.

Introduction

The established chemistry of phosphorus(III)−nitrogen compounds (phosphazanes) involves an extensive series of heterocatenated dimers of type **2**.[1,2] Monomeric halo(imino)-phosphines **1** have been isolated for derivatives involving the bulky Mes* (2,4,6-tri-*tert*-butylphenyl) substituent at nitrogen,[3] which imposes a relative destabilization of the corresponding dimer due to substituent steric strain.[4,5] Few examples of halophosphazane trimers **3** have been reported,[6−8] and in general, cyclic $(R'PNR)_n$ oligomers with $n > 2$ are rare.[8−12] Extended cyclic phosphazanes are only observed with "skeletal stabilization"[11−19]or tethering of cyclodiphos-

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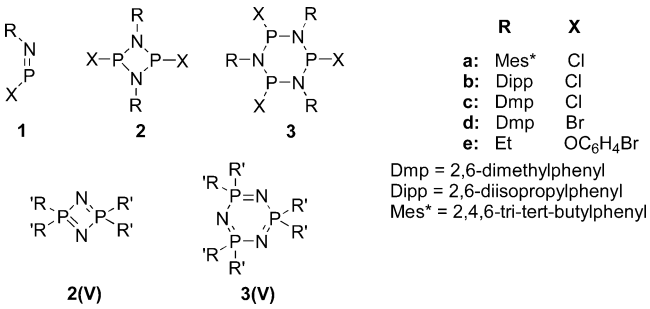
phadiazane units.[20−27] Preference for the diphosphadiazane framework contrasts the wide range of oligomeric arrangements that are well-known for phosphorus(V)−nitrogen compounds (phosphazenes) usually represented by **3(V)**[28] (isomeric with **3**, disregarding exocyclic substituents), while dimeric phosphazenes **2(V)** are very rare.[29,30]



Energetic distinction between cyclic P(III)−N oligomeric options **2** and **3** is likely small, representing a balance between relative ring strain, relative substituent steric strain, and entropy. Recognizing that N−P bonds are susceptible to interchange with N═P multiple bonds by phosphine migration[31] and that some iminophosphines undergo reversible dimerization,[3,5,32] transformations between monomeric, dimeric, trimeric, oligomeric, and polymeric phosphazanes may be achievable. In this context, we now report a ring expansion reaction of dihalodiphosphadiazanes **2** that is promoted by gallium halide, giving a new ionic triphosphazanium tetrachlorogallate. Liberation of gallium chloride by addition of 4-(dimethylamino)pyridine (DMAP) gives the trihalotriphosphatriazane **3**. Structural comparisons between dimers and trimers indicate that the thermodynamic preference for the trimer is governed by the relative flexibility of the P−N framework enabling accommodation of substituent steric strain. The observations highlight the lability of the N−P bond in dihalophosphadiazanes allowing for transformations that formally involve insertion of a monomer **1** into the corresponding dimer **2**.

Experimental Section

General Information. All manipulations were carried out under oxygen- and moisture-free conditions using standard high-vacuum, Schlenk, or drybox techniques. Chemicals and reagents were obtained from Aldrich Chemical Co. All solvents were dried by standard procedures prior to use. Aniline, 2,6-dimethylphenylaniline ($DmpNH_2$), 2,6-diisopropylaniline ($DippNH_2$), gallium chloride, and gallium bromide were all used as received. Phosphorus trichloride and phosphorus bromide were distilled prior to use, while triethylamine was purified by fractional distillation from potassium hydroxide and calcium hydride. $(ClPNPh)_2$[33] and $(ClPNDipp)_2$[34] (**2b**) were prepared as previously reported. Solvent volumes in reaction mixtures are approximate.

Infrared spectra were recorded as Nujol mulls on CsI plates using a Bruker Vector 22 FT-IR and are presented as wavenumber (cm^{-1}) maxima with ranked intensity for each absorption given in parentheses and the most intense peak given a ranking of 1. Melting points were obtained using an electrothermal apparatus. Elemental analyses were performed by Desert Analytics, Tuscon, AZ. Samples for analysis by solution NMR spectroscopy were flame-sealed. Solution ^1H and ^{31}P NMR spectra were obtained at room temperature on a Bruker AC-250 NMR spectrometer. Chemical shifts are reported in ppm relative to a reference standard [$SiMe_4$ (^1H) and 85% H_3PO_4 (^{31}P)], with ^1H spectra calibrated to an internal reference signal ($CHDCl_2$, 5.32 ppm; $CHCl_3$, 7.26 ppm). X-ray diffraction data were obtained on a Bruker PLATFORM diffractometer with a sealed tube generator and a SMART 1000 CCD detector using graphite-monochromated Mo Kα (λ = 0.710 73) radiation on samples cooled to 193(2) K. The structures were solved by direct methods and refined by full-matrix least squares. Unit cell parameters were obtained from the refinement of the setting angles of reflections from the data collection. The choice of space groups was based on systematically absent reflections and was confirmed by the successful solution and refinement of the structures. Crystal data are presented in Table 1, and selected bond lengths and angles are presented in Table 2.

Preparation/Isolation Procedures and Characterization Data. General Method for $(XPNDmp)_2$ (X = Cl, Br). PX_3 and NEt_3 were combined in benzene and cooled in an ice bath, and $DmpNH_2$ was added (15 min). The mixture was warmed to room temperature and stirred for 18 h giving a precipitate that was filtered off and washed twice with benzene (total 100 mL). Removal of the solvent from the combined filtrates under reduced pressure gave a pale orange solid, which was washed with pentane (50 mL), and the white powder was recrystallized in a minimum amount of toluene at −30 °C. Rod-shaped crystals suitable for X-ray diffraction experiments were obtained by allowing a portion of the first filtrate to stand at room temperature for a period of 1 week.

$(ClPNDmp)_2$, 2c. PCl_3 (10.0 mL, 115 mmol), NEt_3 (33.3 mL, 460 mmol), $DmpNH_2$ (14.1 mL, 115 mmol), benzene (500 mL); yield 8.04 g, 21.7 mmol, 37.7%; mp 119−123 °C. Anal. Calcd (found) for $C_{16}H_{18}N_2P_2Cl_2$: C, 51.77 (51.71); H, 4.89 (5.26); N, 7.55 (7.15). NMR: $^{31}P\{^1H\}$ ($CDCl_3$), 210; ^1H ($CDCl_3$), 2.69 (s), 7.12 (s). IR: 414(5), 463(7), 505(6), 533(10), 561(12), 580(18),

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Table 1. Crystal Data

	(ClPNDmp)$_2$, **2c**	(BrPNDmp)$_2$, **2d**	(ClPNDmp)$_3$·C$_6$H$_6$, **3c**	(BrPNDmp)$_3$, **3d**	[(DippN)$_3$P$_3$Cl$_2$][GaCl$_4$]·CH$_2$Cl$_2$, **7b**[GaCl$_4$]
empirical formula	$C_{16}H_{18}Cl_2N_2P_2$	$C_{16}H_{18}Br_2N_2P_2$	$C_{30}H_{33}Cl_3N_3P_3$	$C_{24}H_{27}Br_3N_3P_3$	$C_{37}H_{53}Cl_8GaN_3P_3$
fw	371.16	460.08	634.85	690.13	986.05
cryst system	monoclinic	monoclinic	monoclinic	monclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	11.285(1)	15.772(2)	8.658(1)	15.306(1)	10.469(1)
b (Å)	11.234(1)	11.513(1)	30.316(3)	19.798(1)	13.985(1)
c (Å)	14.393(1)	20.513(2)	11.792(1)	17.934(1)	16.467(1)
α (deg)	90.00	90.00	90.00	90.00	87.237(1)
β (deg)	105.652(1)	104.628(2)	96.593(2)	97.0275(9)	81.353(1)
γ (deg)	90.00	90.00	90.00	90.00	78.866(1)
V (Å^3)	1757.0(2)	3604.3(6)	3074.7(6)	5393.8(5)	2338.2(3)
Z	4	8	4	8	2
D_C (Mg m^{-3})	1.403	1.696	1.371	1.700	1.401
R ($I > 2\sigma(I)$)[a]	0.0487	0.0346	0.0427	0.0357	0.0531
wR (all data)[a]	0.1217	0.0715	0.1144	0.0910	0.0981
goodness-of-fit S[a]	1.036	1.018	1.106	1.027	1.022

[a] $R(F\ [I > 2\sigma(I)]) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR(F^2\ (\text{all data})) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $S\ (\text{all data}) = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ [n = no. of data; p = no. of parameters varied; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program (see Supporting Information)].

Table 2. N−P and P−X Distances (Å), N−P−N Angles (deg), and Sums of Angles at Phosphorus and Nitrogen Centers for Derivatives of **2** [Including (ClPNDipp)$_2$],[34] **3** [Including (EtNPOC$_6$H$_4$Br-4)$_3$],[9] and **7b**[GaCl$_4$]

	(XPNDmp)$_2$ (X = Cl, **2c**; X = Br,[a] **2d**)[b]	(ClPNDipp)$_2$,[34] **2b**		(XPNDmp)$_3$ (X = Cl, **3c**; X = Br,[a] **3d**)[b]	[(DippN)$_3$P$_3$Cl$_2$][GaCl$_4$], **7b**[GaCl$_4$]	[EtNPOR]$_3$,[9] **3e** (cis, trans)[c]
N1−P1	1.703(3)	1.71(3)	N1−P1	1.704(2)	1.697(2)	1.68(1)
	1.708(3)			1.689(3)		1.67(2)
N1−P2	1.713(2)	1.73(1)	N1−P2	1.687(2)	1.703(2)	1.69(2)
	1.702(3)			1.702(3)		1.69(2)
N2−P1	1.703(3)	1.69(1)	N2−P3	1.694(2)	1.656(2)	1.68(1)
	1.708(3)			1.707(3)		1.62(2)
N2−P2	1.704(2)	1.69(2)	N2−P2	1.717(2)	1.736(2)	1.67(1)
	1.706(3)			1.686(3)		1.67(2)
			N3−P3	1.703(2)	1.650(2)	1.68(2)
				1.696(3)		1.63(2)
			N3−P1	1.693(2)	1.753(2)	1.69(1)
				1.713(3)		1.68(2)
P1−X1	2.111(1)	2.071(8)	P1−X1	2.104(1)	2.081(1)	1.67(1)
	2.293(1)			2.308(1)		1.62(2)
P2−X2	2.111(1)	2.085(8)	P2−X2	2.116(1)	2.088(1)	1.65(1)
	2.301(1)			2.286(1)		1.65(2)
			P3−X3	2.136(1)	2.704(1)	1.67(1)
				2.324(1)		1.61(2)
N2−P1−N1	81.6(1)	81.3(7)	N1−P1−N3	101.7(1)	99.4(1)	101.9(8)
	81.4(1)			100.6(1)		99.0(9)
N2−P2−N1	81.3(1)	80.5(7)	N1−P2−N2	100.1(1)	100.8(1)	102.0(7)
	81.6(1)			101.8(1)		103.9(8)
			N2−P3−N3	101.8(1)	105.0(1)	101.2(8)
				101.8(1)		97(1)
Σ(angles P1)	290.0(1)	290.1(7)	Σ(angles P1)	307.5(1)	304.5(9)	302.3(8)
	291.5(1)			307.9(1)		299.0(9)
Σ(angles P2)	290.2(1)	289.8(7)	Σ(angles P2)	305.5(1)	302.6(7)	302.0(8)
	291.3(1)			306.0(1)		300.4(9)
			Σ(angles P3)	303.9(1)		303.1(8)
				305.2(1)		297(1)
Σ(angles N1)	355.5(2)	355(1)	Σ(angles N1)	360.0(1)	359.7(2)	360(1)
	354.7(2)			359.9(2)		359(1)
Σ(angles N2)	355.0(2)	355(1)	Σ(angles N2)	358.1(1)	359.0(2)	358(1)
	354.7(2)			359.3(2)		355(2)
			Σ(angles N3)	359.6(2)	359.6(2)	357(1)
				358.8(2)		356(1)

[a] Two essentially indistinguishable molecules in the asymmetric unit, parameters given for one molecule. [b] Pairs of data are given where the X = Cl value is first below which is the X = Br value. [c] Pairs of data are given where the cis value is first below which is the trans value.

615(20), 740(13), 775(3), 895(1), 920(4), 976(14), 983(15), 1032(16), 1074(17), 1097(9), 1167(11), 1209(2), 1262(8), 1283(10).

(BrPNDmp)$_2$, 2d. PBr_3 (4.0 mL, 42 mmol), NEt_3 (9.1 mL, 130 mmol), $DmpNH_2$ (5.2 mL, 42 mmol), benzene (80 mL); yield 2.0 g, 4.4 mmol, 21%; mp 226−230 °C. Anal. Calcd (found) for $C_{16}H_{18}N_2P_2Br_2$: C, 41.77 (42.14); H, 3.94 (4.19); N, 6.09 (5.83). NMR: $^{31}P\{^1H\}$ ($CDCl_3$), 231; ^1H ($CDCl_3$), 2.74 (s), 7.13 (s). IR: 410(8), 440(1), 496(4), 530(5), 559(13), 586(17), 670(20), 740(15), 770(2), 889(3), 920(7), 977(14), 1033(16), 1099(10), 1167(11), 1207(6), 1247(19), 1261(9), 1287(12), 1581(18).

[(DippN)$_3$P$_3$Cl$_2$][GaCl$_4$], 7b[GaCl$_4$]. A solution of $GaCl_3$ (0.30 g, 1.70 mmol) in dichloromethane (15 mL) was slowly added to a solution of $(ClPNDipp)_2$ (1.25 g, 2.59 mmol) in dichloromethane (15 mL). The orange solution was left to stir overnight, and the solvent was removed in vacuo (static) to give an oil. Addition of hexane (10 mL) followed by slow removal under vacuum gave a froth, which was recrystallized from minimal dichloromethane at 4 °C: yield 0.38 g, 0.46 mmol, 27%; mp 136−139 °C. Anal. Calcd (found) for $C_{36}H_{51}N_3P_3Cl_4Ga$: C, 45.07 (44.77); H, 5.42 (5.36); N, 4.20 (4.41). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): 193 K, 87 (s), 208 (broad singlet); 298 K, 268 (s). IR: 401(12), 427(15), 466(20), 472(16), 488(11), 801(5), 803(4), 849(17), 856(18), 932(19), 962 (2), 970(3), 977 (1), 1006 (13),1041(14), 1095(7), 1152 (10), 1364(9), 1384(8), 1436(6).

General Method for (XPNDmp)$_3$ (X = Cl, Br). $(XPNDmp)_2$ was added to GaX_3, each dissolved in dichloromethane (10 mL), giving an orange solution. After the solution was stirred for 15 h, DMAP was added to give a yellow solution. The solvent was removed in vacuo giving a frothy yellow oil, which was extracted with benzene (20 mL).

(ClPNDmp)$_3$, 3c. $(ClPNDmp)_2$ (0.75 g, 2.0 mmol), $GaCl_3$ (0.31 g, 1.8 mmol), DMAP (0.21 g, 1.8 mmol). Slow removal of solvent (benzene) under a static vacuum gave colorless rod-shaped crystals: yield 0.28 g, 0.50 mmol, 37%; mp 135−138 °C. Anal. Calcd (found) for $C_{24}H_{27}N_3P_3Cl_3$: C, 51.77 (50.74); H, 4.89 (5.07); N, 7.55 (7.33). NMR: $^{31}P\{^1H\}$ (CD_2Cl_2), 111 (s, 2P), 116 (s, 1P); ^1H (CD_2Cl_2), 2.55 (s), 2.74 (s), 7.25 (m). IR: 374(9), 449(3), 509(10), 530(16), 563(20), 578(13), 729(8), 776(5), 802(14), 856(12), 924(17), 964(1), 979(4), 1020(7), 1097(6), 1160(2), 1211(19), 1260(15), 1566(18), 1649(11).

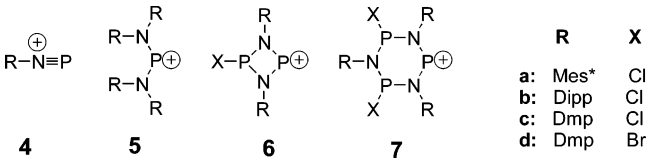
(BrPNDmp)$_3$, 3d. $(BrPNDmp)_2$ (1.00 g, 2.17 mmol), $GaBr_3$ (0.50 g, 1.6 mmol), DMAP (0.25 g, 1.6 mmol). Removal of solvent (benzene) in vacuo gave a pale yellow solid, which was recrystallized from a minimum amount of toluene at −30 °C. The recrystallized product was dissolved in dichloromethane, and vapor diffusion with pentane afforded colorless plate-shaped crystals: yield 0.23 g, 0.33 mmol, 23%; mp 241−243 °C. Anal. Calcd (found) for $C_{24}H_{27}N_3P_3Br_3$: C, 41.77 (40.63); H, 3.94 (4.10); N, 6.09 (5.95). NMR: $^{31}P\{^1H\}$ ($CDCl_3$), 121 (s, 2P), 134 (s, 1P); ^1H (CD_2Cl_2), 2.61 (s), 2.79 (s), 2.82 (s), 2.87 (s). 7.24 (m). IR: 322(10), 426(6), 452(16), 503(15), 528(12), 576(13), 727(9), 747(17), 775(4), 854(8), 890(20), 910(7), 960(1), 975(3), 1023(11), 1096(5), 1156(2), 1260(14), 1562(19), 1648(18).

Phosphorus-31 NMR Studies of Reaction Mixtures in CH_2Cl_2 (Approximately 0.02 M). A 2 equiv amount of $GaCl_3$ was added to **2b** or **2c**, or 2 equiv of $GaBr_3$ was added to **2d**, and the mixtures were stirred for 1 h, followed by addition of 2 equiv of DMAP. The ^{31}P NMR spectrum of each mixture contained only a single signal corresponding to the starting materials **2b**−**d**, respectively.

A 2 equiv amount of $GaCl_3$ was added to 3 equiv of **2b** or **2c**, or 2 equiv of $GaBr_3$ was added to 3 equiv of **2d**, and the mixtures were stirred for 1 h, followed by addition of 2 equiv of DMAP. The ^{31}P NMR spectrum of each mixture contained only two signals corresponding to **3b**−**d**, respectively.

Results and Discussion

Heterolytic cleavage of the P−Cl bonds in Mes*NPCl, **1a**, and chloro(diamino)phosphines is readily achieved by reaction with $AlCl_3$ or $GaCl_3$ to give cations **4a**[35,36] and **5** (R = Me, Et, ^{i}Pr),[37,38] respectively. In this context, dichlorodiphosphadiazanes **2** (X = Cl) offer the possibility of dication formation; however, ^{31}P NMR spectra of reactions between 1,3-dichloro-2,4-di-*tert*-butyldiphosphadiazane, **2** (R = ^{t}Bu, X = Cl), and $AlCl_3$ show the presence of only monochlorodiphosphadiazanium cation **6** (R = ^{t}Bu, X = Cl),[39] independent of reaction stoichiometry. As part of our program to develop polyphosphorus cations with higher charges,[40] we have prepared derivatives of **2** containing aryl substituents of medium steric load (Dipp in **2b**, Dmp in **2c**,**d**) and have examined reactions with GaX_3, which lead to ring expansion demonstrating lability of the heterocyclic N−P framework.



Colorless derivatives of **2 (b−d)** react with gallium halides (GaX_3, X = Cl or Br) on mixing the solids at room temperature to give bright red liquids, which dissolve in CH_2Cl_2 and exhibit a broad signal in the ^{31}P NMR spectrum at approximately 220 ppm (cf.: **2b**, 211 ppm;[34] **2c**, 210 ppm; **2d**, 231 ppm), as well as sharp signals of low relative integration at approximately 90 ppm (tentatively assigned to **4b**,**c**, respectively; cf. **4a**, $\delta(^{31}P)$ range 75−95 ppm)[36] and 270 ppm (tentatively assigned to **6b**−**d**, respectively; cf. **6**, R = ^{t}Bu, X = Cl, $\delta(^{31}P) \sim 270$ ppm, coalescence above RT (room temperature)).[39] The spectra are dependent on reaction stoichiometry and temperature; however, it has not been possible to determine coalescence points.

Removal of solvent from reaction mixtures of **2b** with $GaCl_3$ at a stoichiometry of 3:2 gives an oil, from which a crystalline material has been obtained and characterized as $[(DippN)_3P_3Cl_2][GaCl_4]$, **7b**[$GaCl_4$], illustrated in Figure 1.[5] Although isolated in modest yield (27%), the formation of **7b**[$GaCl_4$] can be rationalized by eq 1, representing an unusual ring expansion process involving cleavage of a number of N−P bonds and transfer of an $[DippNP]^+$ fragment between molecules of **2b**, as well as abstraction of Cl^- by $GaCl_3$. Reaction of **7b**[$GaCl_4$] with DMAP gives the corresponding trihalotriphosphatriazane **3b** (eq 2), representing the preferential formation of the DMAP−$GaCl_3$ adduct, consequential release of chloride ion from the complex anion [$GaCl_4^-$], and association of chloride with the phosphenium site of **7b**. Preferential interaction of DMAP with the relatively strong Lewis acidic $GaCl_3$ (from [$GaCl_4$]) is

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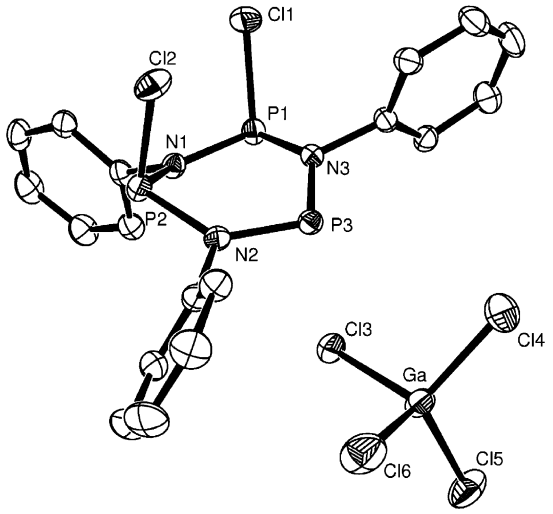
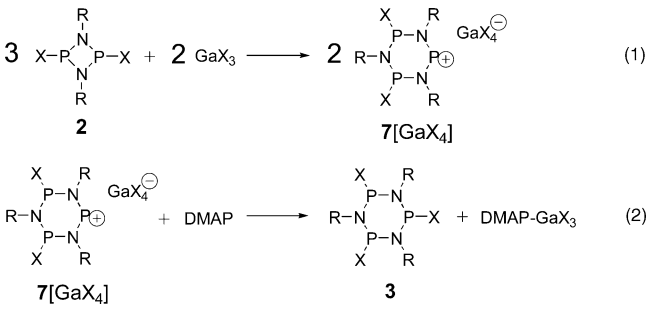


Figure 1. Solid-state structure of $[(DippN)_3P_3Cl_2][GaCl_4]$, **7b**$[GaCl_4]$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and isopropyl groups are not shown.

expected, despite the demonstrated Lewis acceptor behavior for phosphenium sites of the type present in **7b**.[41]



Phosphorus-31 NMR spectroscopic studies of analogous reaction mixtures containing 3 equiv of **2b**−**d** with 2 equiv of GaX_3 (X = Cl for **b** and **c**, X = Br for **d**) followed by the addition of 1 equiv of DMAP show two signals with relative intensity of 1:2 indicating quantitative transformation to **3b** ($\delta(^{31}P)$ 110, 116 ppm), **3c** ($\delta(^{31}P)$ 111, 116 ppm), and **3d** ($\delta(^{31}P)$ 121, 134 ppm), respectively (eq 2). Analogous reaction mixtures containing $(ClPNPh)_2$ show numerous phosphorus-containing species that could not be isolated, indicating that the essentially quantitative process observed in the transformation of **2b**−**d** to **3b**−**d** is controlled by the steric limitations imposed by the relatively bulky Dipp and Dmp substituents.

Reaction mixtures containing 1 equiv of **2b**−**d** with 2 equiv of GaX_3 (X = Cl for **b** and **c**, X = Br for **d**), followed by the addition of 2 equiv of DMAP show quantitative reformation of the starting diphosphadiazane **2b** ($\delta(^{31}P)$ 211 ppm), **2c** ($\delta(^{31}P)$ 210 ppm), and **2d** ($\delta(^{31}P)$ 231 ppm), respectively. We conclude that derivatives of **7** predominantly exist at the appropriate stoichiometry of 3:2 and a relative increase in GaX_3 either impedes the ring expansion process or dissociates the six-membered heterocycle **7**.

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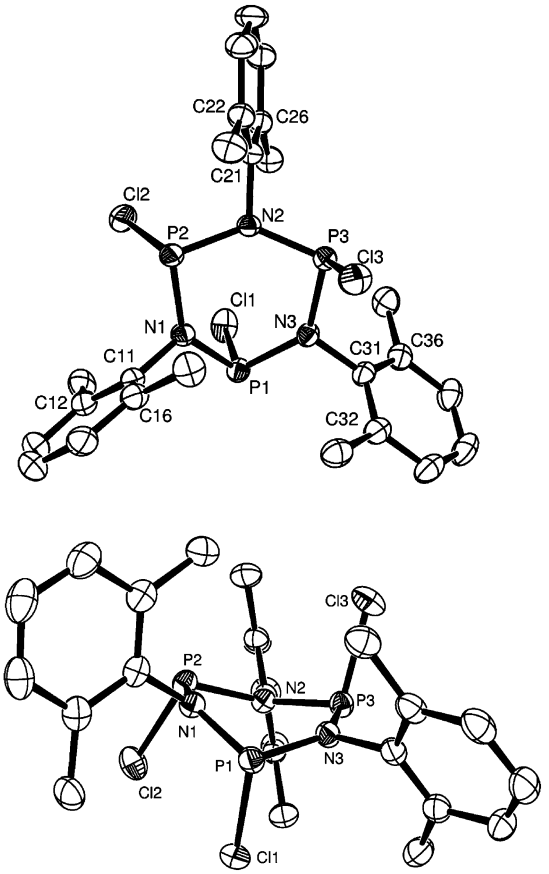

Figure 2. Two views of $(ClPNDmp)_3$, **3c**, in the solid state. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are not shown.

Single-crystal X-ray diffraction data for **7b**$[GaCl_4]$, **3c**,**d**, and **2c**,**d** are presented in Table 1, and selected structural parameters (N−P and P−X distances, N−P−N angles, sum of angles at nitrogen and phosphorus centers) are listed in Table 2, together with corresponding parameters for **2b**[34] and for the rare example of a trimeric phosphazane $(EtNPOC_6H_4$-Br-4$)_3$,[9] **3e**. A trans configuration of halogens is observed for both **3c**,**d** in the solid state (illustrated for **3c** in Figure 2) and in solution, as demonstrated by the two distinct signals observed in the ^{31}P NMR spectra, with relative intensity of 1:2. There is no evidence of the cis isomer in the reaction mixtures, in contrast to previous reports of both cis and trans configurations for $(EtNPOC_6H_4Br$-4$)_3$, **3e**.[9] Interestingly, $^2J_{PP}$ coupling is not observed for **3b**−**d** over the temperature range of 80 to −80 °C. The dimers **2b**−**d** adopt a cis halogen configuration with respect to the almost planar PNPN square (e.g. Figure 3). In all derivatives of **2** and **3**, the endocyclic angles at the essentially planar nitrogen centers are larger than those at the pyramidal phosphorus centers. The geometry of each environment is indicated by the sums of the three angles, which define an almost planar geometry at nitrogen and a distinctly pyramidal geometry at phosphorus (substantially less than 360°). The nitrogen centers in derivatives of **2** are slightly distorted from planarity, perhaps due to the combination of ring strain and substituent steric strain. These factors may also be responsible for the observed trans configuration for derivatives of **3**.

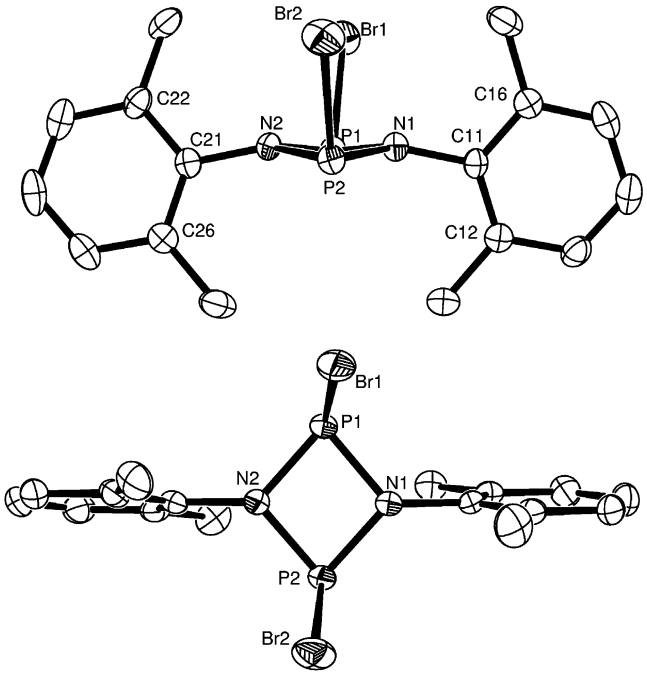

Figure 3. Two views of $(BrPNDmp)_2$, **2d**, in the solid state. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are not shown.

Although the P−Cl distances cannot be distinguished in the structure of **3c** (Figure 2), the trans-configured P3−Cl3 in **7b**[$GaCl_4$] (Figure 1) is dramatically longer [2.704(1) Å] than the cis-configured P−Cl distances [2.081(1), 2.088(1) Å] and is longer than a typical P−Cl distance [cf. PCl_3, 2.038(6) Å].[42] This distinction in P3−Cl3 for **7b**[$GaCl_4$] is due to interaction of Cl3 with gallium, although the Cl3−Ga distance is only slightly longer [2.249(1) Å] than the other three [Cl−Ga 2.149(1), 2.150(1), 2.156(1) Å]. Consistently, the N−P distances in **3c**,**d** are essentially indistinguishable, while N−P3 distances in **7b** [N2−P3 1.656(2) and N3−P3 1.650(2) Å] are significantly shorter than the neighboring bonds [N2−P2 1.736(2) and N3−P1 1.753(2) Å]. Moreover, the endocyclic angle at P3 [105.0(1)°] in **7b**[$GaCl_4$] is relatively wide compared with those at P1 and P2 and the corresponding angles in **3c**,**d**. Therefore, we assign an ionic formulation for **7b**[$GaCl_4$] and describe the cation **7b** as an assembly of a P1−N1−P2 phosphazane unit and a N2−P3−N3 "diaminophosphenium" unit, representing a six-membered analogue of **6**.[39] In this context, the relatively short N2−P3 and N3−P3 distances implicate significant π interaction at the phosphenium site P3.

We envisage halide abstraction from **2** to give **6** as the initial step of the ring expansion process, but it is not yet possible to distinguish between subsequent steps involving ring opening, coordination propagation, or elimination of **1**. The potential formation of a monomeric intermediate prompts consideration of a monomer−dimer equilibrium, which has been demonstrated for Mes*NPOTf[5] and is imposed by substituent steric strain.[4] In this context, the orange color of the reaction mixtures of **2** with GaX_3 and the observation of a signal at 90 ppm in the ^{31}P NMR spectra suggest the presence of [RNP][GaX_4], **4**[GaX_4], which may insert into the dimer **2**.

Table 3. X−N−P−C Torsional Angles (deg) for **2c**,**d** and **3c**,**d**

	$(ClPNDmp)_2$, **2c**	$(BrPNDmp)_2$, **2d**	$(ClPNDmp)_3$, **3c**	$(BrPNDmp)_3$, **3d**
X1−P1−N1−C11	90.1(3)	87.7(3)	119.5(1)	97.0(2)
X2−P2−N1−C11	94.6(3)	94.2(3)	97.3(1)	120.8(2)
X1−P1−N2−C21	94.7(3)	95.5(3)		
X2−P2−N2−C21	90.3(3)	88.8(3)	65.4(1)	103.4(2)
X3−P3−N2−C21			92.4(1)	66.3(2)
X1−P1−N3−C31			97.4(1)	67.6(2)
X3−P3−N3−C31			77.4(2)	84.3(2)

The thermodynamic preference for trimeric phosphazanes over the more familiar dimeric analogues due to the imposition of sterically loaded substituents such as Dipp and Dmp is counterintuitive. Substituent steric strain is expected to favor monomers or smaller oligomers in which the substituents are spatially less restricted. We conclude that the substituent steric strain in **2b**−**d** destabilizes the dimer relative to the corresponding trimer **3** by virtue of relative N−P framework flexibility. The greater substituent steric strain in the dimers **2** is evidenced (Table 2) by slight distortions from planarity at the nitrogen centers (sum of angles at N <356°), which results from interactions between the cis bromide substituents and the methyl groups at C16 and C22, as shown in Figure 3. In comparison, the environments for nitrogen in the trimers **3** are closer to planar (sum of angles at N >358°). More apparent are the differences in torsional angles about the N−P bonds (Table 3), which reveal the relative orientation of X and the ipso carbon center. The dimers exhibit X−P−N−C torsional angles all close to 90°, while the corresponding trimers demonstrate a more flexible framework with distortions (from 90°) as large as 29°. The consequences of these distortions include the twist of the aryl substituent away from the halide for C22 in Figure 2, which is limited in the more restricted frame of the dimers as shown in Figure 3. The boat-shaped frameworks of the trimers reveal a nonsymmetric twisting of the aryl substituents and a nonsymmetric orientation of the halide substituents minimizing distortions from planarity at each nitrogen center without compromising the accommodation of substituent steric strain. We associate these subtle structural distinctions between dimer and trimer with the relative thermodynamic preference for the trihalotriphosphatriaryltriazanes over the dihalodiphosphadiaryldiazanes.

Conclusions

Deep orange reaction mixtures of dimeric dihalodiphosphadiazanes **2** with GaX_3 become colorless on addition of DMAP, and the corresponding trimeric **3** trihalophosphatriazanes have been isolated. An unusual cyclophosphazanium tetrachlorogallate salt [$(DippN)_3P_3Cl_2$][$GaCl_4$] has been isolated and represents an intermediate in the disproportionation process. The lability of the N−P bond in derivatives of **2** is imposed by appropriate selection of substituents (R) with medium steric loading that thermodynamically destabilizes the dimer **2** with respect to the corresponding trimer **3**, but the substituents have insufficient steric bulk to favor the monomer **1**. This ring expansion reaction is analogous

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to the gallium chloride induced ring-opening polymerization of a thionylphosphazene[43] but represents an interesting contrast to the ring contraction of cyclocarbophosphazenes also facilitated by gallium chloride.[44] As phosphazane chemistry has been essentially limited to dimeric frameworks, the manipulation of substituent steric strain to modify the relative stability of the phosphazane framework in favor of the trimer represents a new opportunity for diversification.

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Supporting Information Available: Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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