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Synthesis of *cyclo*-2,4,6-Triarsa-1,3,5-triazanes from *cyclo*-2,4-Diarsa-1,3-diazanes Demonstrating the General Influence of Substituent Steric Strain on the Relative Stability of Pnictazane Oligomers

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2,4-Dichloro-1,3-diaryl-*cyclo*-2,4-diarsa-1,3-diazanes (aryl = 2,6-dimethylphenyl, Dmp, or 2,6-diisopropylphenyl, Dipp) have been transformed into the corresponding 2,4,6-trichloro-*cyclo*-2,4,6-triarsa-1,3,5-triazanes on reaction with $GaCl_3$ followed by 4-(dimethylamino)pyridine (DMAP). The nitrogen bound Dmp and Dipp substituents impose "medium" substituent steric strain on the heterocycles influencing the relative thermodynamic stability of potential oligomers in favor of the trimers. This ring expansion disproportionation reaction is initiated by chloride ion abstraction, and the intermediate 2,4-dichloro-1,3,5-tris(2,6-diisopropylphenyl)-*cyclo*-2,4-diarsa-1,3,5-triazane-6-arsenium tetrachlorogallate has been isolated and structurally characterized. Subsequent reaction with 4-(dimethylamino)pyridine (DMAP) effects release of chloride ion from the gallate anion and consequential formation of a covalent As–Cl bond in the trimer. The observations are analogous to those for the phosphorus derivatives demonstrating a general applicability of this new synthetic procedure for the development and diversification of cyclopnictazane chemistry.

Introduction

The N−P heterocatenated cyclophosphazenes $(R_2PN)_n$ are known to exist in a wide range of ring sizes, and some have been transformed into useful polymeric materials.[1−3] Analogous compounds ("cyclopnictazenes") containing the other pnictogen elements (As, Sb, Bi,) are rare.[4−7] Cyclophosphazanes represent $(RPNR')_n$ isomers of cyclophosphazenes and are known for $n = 2-4$,[8−20] but examples of dimers $(RPnNR')_2$ have been reported for all of the heavier pnictogens (Pn = P,[10−13] As,[21−24] Sb,[25−32] Bi[33,34]), including an homologous series,[13] highlighting the potential for extrapolation of synthetic procedures from phosphorus to bismuth.

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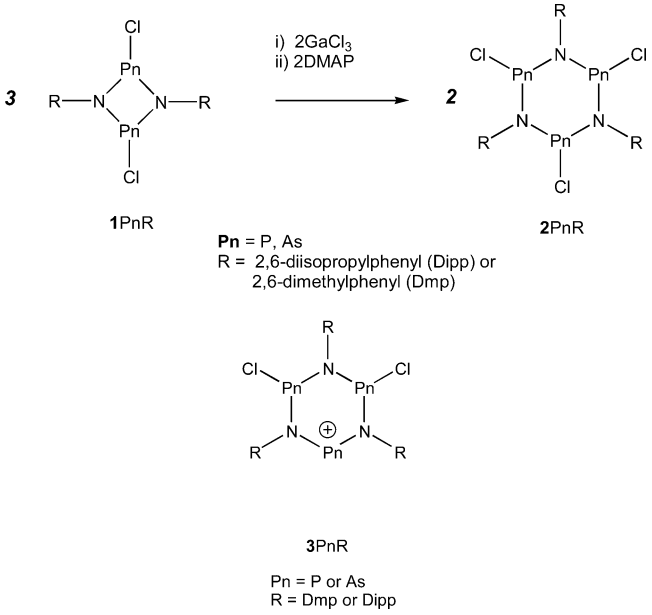
We envisage the potential for ring-opening oligomerization and polymerization (that has been well established for cyclophosphazenes[1,2]) of these cyclodipnictadiazanes and the possibility to acquire an array of NP, NAs, NSb, and NBi polymer backbones, with a consequential variety of properties. Therefore, we are devising general synthetic methods for cyclopnictazanes and have exploited the steric influence of organic substituents at nitrogen to manipulate the relative thermodynamic stability of the pnictazane oligomers. The imposition of large substituent steric strain[35] in derivatives of $(RPNR')_2$ can destabilize the dimer enthalpically with respect to the monomer.[36] However, we have noted that the medium-sized substituents 2,6-dimethylphenyl- (Dmp) and 2,6-diisopropylphenyl- (Dipp) provide suitable steric strain to favor and promote the formation of trimeric cyclophosphazanes **2**P from the corresponding dimers **1**P.[14] We now illustrate the generality of this substituent steric tuning of cyclopnictazane oligomerization with the preparation and characterization of analogous heterocycles for Pn = As. In addition, six-membered cationic intermediates **3**As have been isolated and comprehensively characterized.



Experimental Section

General Information. All manipulations were carried out under oxygen- and moisture-free conditions using standard Schlenk or drybox techniques. Chemicals and reagents were obtained from Aldrich Chemical Co. All solvents were dried on an MBraun solvent purification system and stored over molecular sieves prior to use. 4-(Dimethylamino)pyridine (DMAP), 2,6-dimethylaniline (Dmp-NH_2), and 2,6-diisopropylaniline (DippNH_2) were used as received. Arsenic trichloride was distilled and gallium chloride sublimed prior to use, while triethylamine was purified by fractional distillation from potassium hydroxide and calcium hydride. 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 Electro-thermal apparatus. Elemental analyses were performed by Desert Analytics, Tuscon, AZ. Solution ^1H NMR spectra were obtained at room temperature on a Bruker AC-250 NMR spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ and are calibrated to an internal reference signal of $CHCl_3$, 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 Å) 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 $(RNAsCl)_2$ (1AsR; R = Dmp, Dipp). RNH_2 was added slowly over 10 min to an ice-cooled solution of $AsCl_3$ and NEt_3 in benzene (~300 mL). A yellow precipitate formed almost immediately. The solution was stirred for 18 h and then filtered and concentrated by removal of solvent in vacuo. Addition of pentane gave a white precipitate that was separated from the yellow solution, dried, and redissolved; vapor diffusion of pentane into a CH_2Cl_2 solution (R = Dmp) or slow solvent evaporation of benzene (R = Dipp) yielded plate crystals.

$(DmpNAsCl)_2$ (1AsDmp): DmpNH_2 (7.3 mL), $AsCl_3$ (3.0 mL), NEt_3 (10 mL); yield 1.7 g (14%, not optimized); mp 207−209 °C; ^1H NMR ($CDCl_3$) 2.76 (s), 7.12 (m); IR 489 (11), 521 (5) 699 (4), 774 (3), 810 (1), 882 (6), 914 (15), 974 (12), 1030 (10), 1096 (7), 1166 (9), 1203 (2), 1256 (8), 1535 (14), 1587 (13), 1624 (20), 1748 (19), 1867 (18), 1944 (17). Anal. Calcd (found) for $C_{16}H_{18}N_2As_2Cl_2$: C, 41.86 (42.89); H, 3.95 (4.78); N, 6.10 (6.11).

$(DippNAsCl)_2$ (1AsDipp): DippNH_2 (6.7 mL), $AsCl_3$ (5.0 mL), NEt_3 (13 mL); yield 3.4 g (34%, not optimized); mp 231−234 °C;

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Table 1. Crystal Data

param	**1**AsDmp	**1**AsDipp.2C$_6$H$_6$	**2**AsDmp	**2**AsDipp	[**3**AsDipp][GaCl$_4$]·CH$_2$Cl$_2$
empirical formula	$C_{16}H_{18}N_2As_2Cl_2$	$C_{36}H_{46}N_2As_2Cl_2$	$C_{24}H_{27}N_3As_3Cl_3$	$C_{36}H_{51}N_3As_3Cl_3$	$C_{37}H_{53}N_3P_3Cl_8Ga$
fw	459.06	727.49	634.85	856.91	1117.90
cryst system	monoclinic	orthorhombic	monoclinic	monclinic	triclinic
space group	$P2_1/c$	Pnma	$I2/a$	$P2_1/n$	$P\bar{1}$
a (Å)	15.591(1)	22.845(1)	31.883(3)	12.305(1)	10.508(1)
b (Å)	11.425(1)	10.217(1)	9.263(1)	21.386(2)	14.803(1)
c (Å)	20.719(1)	15.694(2)	18.738(1)	16.328(1)	16.591(1)
α (deg)					87.36(1)
β (deg)	104.25(1)		96.36(1)	111.85(1)	81.20(1)
γ (deg)					79.07(1)
V (Å^3)	3576.8(4)	3663.0(4)	5499.9(8)	3955.7(8)	2381.9(2)
Z	8	4	8	4	2
D_C (Mg m^{-3})	1.705	1.319	1.663	1.439	1.559
R ($I > 2\sigma(I)$)[a]	0.0367	0.0337	0.0648	0.0495	0.0317
wR (all data)[a]	0.0.690	0.0652	0.1100	0.0752	0.0742
goodness-of-fit S[a]	1.045	1.053	1.020	1.034	1.049

[a] $R(F\ [I > 2\sigma(I)]) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2\ [\text{all data}]) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; S (all data) $= [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ [n = no. of data; p = no. 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. Selected Bond Lengths (Å) and Angles (deg) for Derivatives of **1**−**3**

param	(DmpNAsCl)$_2$ (**1**AsDmp)	(DippNAsCl)$_2$ (**1**AsDipp)	(DmpNAsCl)$_3$ (**2**AsDmp)	(DippNAsCl)$_3$ (**2**AsDipp)	(MeNAsCl)$_3$[38] (**2**AsMe)	[Dipp$_3$N$_3$As$_3$Cl$_2$][GaCl$_4$] ([**3**AsDipp][GaCl$_4$])	[Dipp$_3$N$_3$P$_3$Cl$_2$][GaCl$_4$][14] ([**3**PDipp][GaCl$_4$])
N1−Pn1	1.841(2)	1.845(1)	1.834(3)	1.848(2)	1.79	1.829(2)	1.697(2)
N(2/3)−Pn1	1.847(2)	1.843(1)	1.836(3)	1.831(2)	1.85	1.881(2)	1.753(2)
N1−Pn2	1.838(2)	1.845(1)	1.846(3)	1.826(2)	1.83	1.834(2)	1.703(2)
N2−Pn2	1.842(2)	1.843(1)	1.826(3)	1.835(2)	1.88	1.864(2)	1.736(2)
N2−Pn3			1.828(3)	1.827(2)	1.76	1.793(2)	1.656(2)
N3-Pn3			1.829(3)	1.837(2)	1.86	1.786(2)	1.650(2)
N−Pn1−N	79.7(1)	79.9(1)	100.2(1)	99.5(1)	102.5	98.4(1)	99.4(1)
Pn1−Cl1	2.243(1)	2.239(1)	2.255(1)	2.230(1)	2.28	2.207(1)	2.081(1)
Pn2−Cl2	2.244(1)	2.239(1)	2.245(1)	2.270(1)	2.24	2.209(1)	2.088(1)
Pn3−Cl3			2.232(1)	2.235(1)	2.28	2.708(1)	2.704(1)
N−Pn2−N	80.0(1)	79.9(1)	98.5(2)	101.4(1)	99.7	99.1(1)	100.8(1)
N−Pn3−N			100.7(1)	100.3(1)	105.5	103.8(1)	105.0(1)
Σ° at N1	353.9(1)	352.8(1)	354.7(3)	356.6(2)	359.1	359.4(1)	359.7(2)
Σ° at N2	354.3(2)	352.1(1)	359.9(2)	359.5(2)	359.6	358.8(1)	359.0(2)
Σ° at N3			360.0(2)	359.4(2)	358.3	358.6(1)	359.6(2)
Σ° at Pn1	258.2(1)	284.6(1)	300.2(1)	301.4(1)	303.9	301.5(1)	304.5(9)
Σ° at Pn2	284.7(1)	284.6(1)	299.1(1)	302.4(1)	295.2	298.1(1)	302.6(7)
Σ° at Pn3			300.3(1)	300.5(1)	301.1		

^{1}H NMR ($CDCl_3$) 1.345 (d), 4.08 (m), 7.28 (s); IR 329 (4), 354 (2), 419 (11), 455 (15), 517 (13), 702 (19), 715 (13), 788 (1), 828 (6), 873 (9), 893 (12), 933 (17), 1041 (18), 1055 (14), 1101 (8), 1191 (3), 1241 (7), 1316 (5), 1384 (10), 1578 (20). Anal. Calcd (found) for $C_{24}H_{34}N_2As_2Cl_2$: C, 50.46 (50.36); H, 6.00 (5.75); N, 4.90 (5.06).

General Method for [R$_3$N$_3$As$_3$Cl$_2$][GaCl$_4$] ([3AsR][GaCl$_4$] R = Dmp, Dipp). (RNAsCl)$_2$ and $GaCl_3$ were combined and dissolved in CH_2Cl_2 (∼2 mL), immediately forming a dark red solution, which faded to light orange after hours. Vapor diffusion of pentane into CH_2Cl_2 gave orange plate crystals.

[Dmp$_3$N$_3$As$_3$Cl$_2$][GaCl$_4$] ([3AsDmp][GaCl$_4$]): (DmpNAsCl)$_2$ (0.20 g), $GaCl_3$ (0.052 g); yield 0.12 g (48%); mp 85−95 °C; IR 445 (16), 487 (8), 523 (3), 551 (17), 628 (14), 640 (15), 700 (7), 718 (6), 736 (9), 874 (1), 914 (4), 980 (12), 1025 (11), 1096 (5), 1164 (2), 1262 (10), 1567 (15), 1799 (20), 1875 (19), 1954 (18). Anal. Calcd (found) for $C_{24}H_{27}N_3As_3Cl_6Ga$: C, 33.34 (33.51); H, 3.15 (3.39); N, 4.86 (4.61).

[Dipp$_3$N$_3$As$_3$Cl$_2$][GaCl$_4$] ([3AsDipp][GaCl$_4$]): (DippNAsCl)$_2$ (0.10 g), $GaCl_3$ (0.021 g); yield 0.049 g (40%); mp 182−185 °C; IR 463 (19), 520 (1), 537 (9), 575 (17), 693 (13), 737 (8), 799 (4), 839 (14), 877 (16), 932 (5), 1037 (7), 1053 (12), 1097 (3), 1159 (2), 1180 (10), 1234 (15), 1264 (11), 1314 (18), 1385 (16), 1581 (20). Anal. Calcd (found) for $C_{36}H_{51}N_3As_3Cl_6Ga$: C. 41.86 (41.19); H, 4.98 (4.75); N, 4.07 (3.60).

General Method for (RNAsCl)$_3$ (2AsR; R = Dmp, Dipp). (RNAsCl)$_2$ and $GaCl_3$ were combined and dissolved in toluene (∼3 mL); the formation of a dark red solution was immediate but faded after 2 h, with stirring for 18 h. Addition of DMAP gave a light yellow solution. Partial removal of the solvent in vacuo deposited a yellow oil, which was separated from the solution.

(DmpNAsCl)$_3$ (2AsDmp): (DmpNAsCl)$_2$ (0.300 g), $GaCl_3$ (0.0767 g), DMAP (0.052 g). The solvent was removed under vacuum to give a white solid, which was dissolved in minimal CH_2Cl_2, and vapor diffusion with pentane gave rod shaped crystals: yield 0.140 g (47%); mp 215−217 °C; ^{1}H NMR ($CDCl_3$) 2.59 (s), 2.69 (s), 2.74 (s), 2.79 (s), 7.20 (s), 7.22 (s); IR 310 (1), 336 (3), 384 (9), 449 (14), 524 (9), 534 (19), 700 (11), 718 (8), 782 (5), 868 (2), 915 (10), 979 (15), 1025 (12), 1098 (6), 1163 (4), 1256 (13), 1559 (17), 1628 (18), 1797 (20), 1954 (16). Anal. Calcd (found) for $C_{24}H_{27}N_3As_3Cl_3$: C, 41.86 (41.59); H, 3.95 (3.94); N, 6.10 (5.87).

(DippNAsCl)$_3$ (2AsDipp): (DippNAsCl)$_2$ (0.150 g), $GaCl_3$ (0.090 g), DMAP (0.065 g). The solution was filtered through a small column of silica, which was washed repeatedly with toluene (∼1 mL). Slow solvent evaporation of the toluene gave plate

crystals: yield 0.065 g (43%); mp 244−247 °C; ^{1}H NMR ($CDCl_3$) 1.14 (d), 1.28−1.39 (m), 3.49 (sep), 3.83 (sep), 3.99 (sep), 4.10 (sep), 7.32−7.41 (m); IR 303 (6), 327 (16), 355 (4), 425 (7), 523 (11), 748 (18), 800 (2), 838 (9), 877 (1), 933 (13), 1036 (12), 1052 (15), 1098 (5), 1159 (3), 1235 (16), 1255 (17), 1310 (14), 1346 (8), 1365 (8), 1592 (20). Anal. Calcd for $C_{36}H_{51}N_3As_3Cl_3$ (found): C, 50.46 (49.65); H, 6.00 (5.74); N, 4.90 (4.85).

Discussion

Discovery and development of new polymeric materials involving elements of group 15 requires realization of effective and versatile synthetic procedures and understanding of processes relating monomers, dimers, and oligomers. Compounds and materials containing phosphorus can be monitored by the sensitive ^{31}P NMR probe, but elucidation of the chemistry for compounds of As, Sb, and Bi is less efficient. Therefore, comparisons in reactivity between homologous series of compounds are vital. In this context, synthetic methodologies devised for phosphorus can sometimes be extrapolated to analogous compounds for arsenic, antimony, and bismuth.

We have embarked on the development of processes that provide access to oligomeric pnictazanes with the ultimate goal of discovering new polymeric materials offering a series of chemically varied but related backbones. Cyclodipnictadiazanes are known for all pnictogens and represent potential starting materials for ring-opening oligomerization and polymerization. In this context, we have recently discovered a high yield ring expansion reaction for cyclodiphosphadiazanes **1**P to give the cyclotriphosphatriazanes **2**P,[14] demonstrating the influence of substituent steric strain imposed by Dmp and Dipp on the relative stability of the oligomers. This process has now been extrapolated to the analogous arsenic derivatives providing high yield preparations of **2**As.

As first recognized by Olah for alkyl derivatives, cyclodiarsadiazanes **1**As are readily prepared by direct addition of excess primary amine to $AsCl_3$.[37] This process can be facilitated and generalized in the presence of NEt_3, and we have exploited this to obtain the new derivatives **1**AsDmp and **1**AsDipp (see below for discussion of structural and spectroscopic features). Both derivatives of **1**As react rapidly with 0.66 equiv of $GaCl_3$ to give dark red solutions, and crystalline materials have been isolated and characterized as [**3**AsR][$GaCl_4$]. In addition, crystals of [**3**AsDipp][$GaCl_4$] were suitable for X-ray crystallography studies (Figure 1). The cation [**3**AsDipp] is a six-membered As−N heterocatenated ring with two chloroarsine centers and one arsenium center, and its formation can be described as a ring expansion disproportionation that is induced by chloride ion abstraction.

Equimolar combinations of DMAP and [**3**As][$GaCl_4$] (including in situ mixtures of **1**As with 0.66 equiv of $GaCl_3$) give yellow solutions, from which the corresponding cyclotriarsatriazanes **2**As have been isolated. The reactions are envisaged to involve release of chloride ion from the gallate anion by formation of DMAP−$GaCl_3$ and consequential formation of a covalent As−Cl bond in **2**As. While the reaction stoichiometry (3:2 **1**As:$GaCl_3$) is appropriate for the formation of [**3**As][$GaCl_4$], the ring expansion process is facilitated by increasing the relative amount of $GaCl_3$, from 0.66 to 2 equiv, given suitable reactions times (>2 h) before addition of DMAP. Addition of DMAP to the reaction mixture after a short (<30 min) reaction time gives **1**As quantitatively. We speculate that the increase in the stoichiometric ratio of $GaCl_3$ promotes the formation of [$RNAs^+$] by chloride ion abstraction and ring cleavage, and drives the equilibrium toward the six-membered heterocyclic cation **3**As.

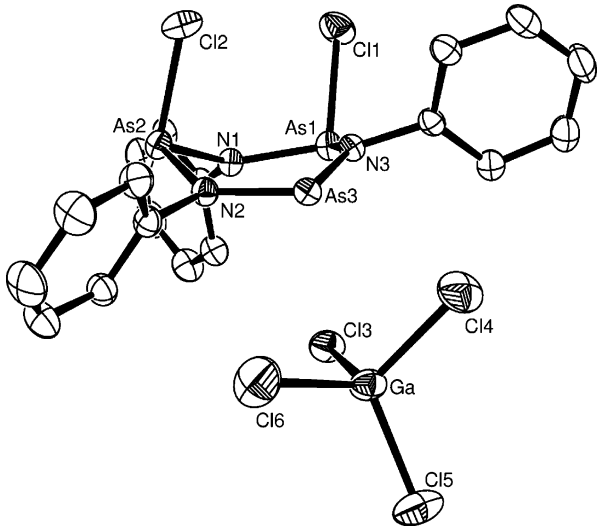

Figure 1. Solid-state structure of [**3**AsDipp][$GaCl_4$]. Hydrogen atoms and isopropyl groups have been omitted. Elipsoids are drawn at 50%.

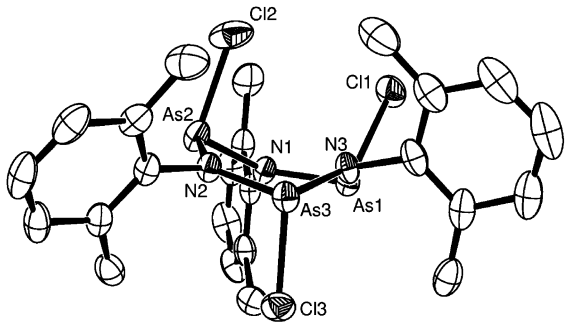

Figure 2. Solid-state structure of **2**AsDmp. Hydrogen atoms have been omitted. Elipsoids are drawn at 50%.

Selected solid-state structural features for **1**AsDmp, **1**AsDipp, **2**AsDmp, **2**AsDipp, and [**3**AsDipp][$GaCl_4$] are listed in Table 2, together with analogous features for **2**AsMe,[38] representing the only previous structural report of an arsazane trimer. Both **1**AsDmp and **1**AsDipp adopt a syn configuration of the chlorine substituents, consistent with the phosphorus analogues **1**PDmp[14] and **1**PDipp[39] and previous structural reports for other derivatives of **1**As,[21,24] although one derivative of **1**As with R = $C_6H_2(CF_3)_3$ exhibits an anti configuration.[22] The geometries at nitrogen and arsenic in **1**AsDmp and **1**AsDipp are distinguished by the sums of the three angles at each site ($\Sigma°$), defining an almost planar

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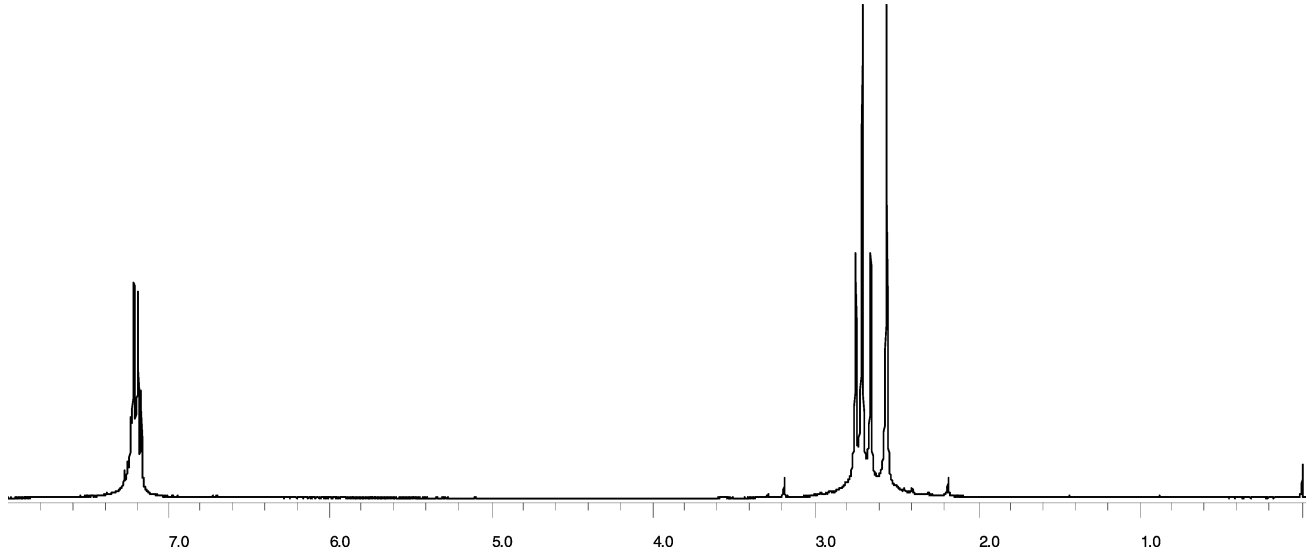
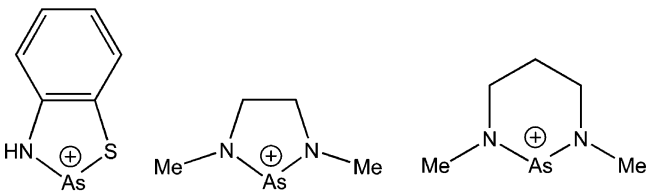


Figure 3. ^{1}H NMR spectrum of **2**AsDmp in $CDCl_3$ at 298 K.

geometry at each nitrogen center (almost 360°; Table 2) and a distinctly pyramidal geometry at each arsenic center (substantially less than 360°). The slight distortion of the nitrogen centers from planarity is due to a combination of ring strain and substituent steric strain.

As for [**3**PDipp][$GaCl_4$],[14] the solid-state structure of [**3**AsDipp][$GaCl_4$] (Figure 1) is distinctly ionic with two covalent As−Cl bonds [As−Cl 2.207(1) and 2.209(1) Å] in a syn configuration about the six-membered As_3N_3 heterocyclic frame and a long anti-configured As3---Cl3 contact [2.708(1) Å] representing the closest interaction between cation and complex anion. The N−As3 distances are correspondingly distinct and are shorter [1.793(2) and 1.786(2) Å] than the other four N−As bonds in the heterocycle [1.829(2), 1.834(2), 1.864(2), 1.881(2) Å], highlighting cation **3**As as an arsazane/arsenium hybrid and indicating a significant π interaction in the N−As3 bonds. In this context, the N2−As3 and N3−As3 bonds compare with those in previously reported examples of azarsenium salts [**4**, 1.776(4) Å;[40] **5**, 1.752(5), 1.949(4) Å, this cation adopts a dimeric arrangement in the solid-state involving intermolecular N−As interactions that effect disruption of one N−As π interaction;[41,42] **6**, 1.68(3), 1.67(2)].[42]



4 **5** **6**

Interesting similarities and distinctions are apparent between **2**PDmp,[14] $(DmpNPBr)_3$,[14] and **2**AsDmp (Figure 2). All adopt an anti configuration of the halogens that is maintained in solution. Four distinct *ortho*-methyl signals in the ^{1}H NMR spectra of $(DmpNPBr)_3$ and **2**AsDmp (Figure 3), with relative intensity of 1:2:1:2, suggest restricted rotation of the 2,6-dimethylphenyl substituents. In contrast, **2**PDmp[14] exhibits only two signals in the ^{1}H NMR spectrum consistent with free rotation about the N−C bonds.

A combination of ring strain and substituent steric strain is likely responsible for the preferred anti configuration in derivatives of **2**, which enables maintenance of the almost planar geometry at each nitrogen center and the distinctly pyramidal geometry at each arsenic or phosphorus center (substantially less than 360°; Table 2). All bond lengths (N−As, N−P, As−Cl, and P−Cl) are essentially identical with those observed in the corresponding dimers and are representative of single bonds.

Although numerous mechanistic pathways can be considered for the disproportionation of **1**Pn to **2**Pn, dissociation of the dimer to provide the corresponding monomer is consistent with the observed equilibrium between Mes*NPOTf and $(Mes*NPOTf)_2$, which have been isolated as a mixture in the solid state.[36] Isolation of the cationic heterocyclic intermediates **3**PDipp[14] and **3**AsDipp indicates that $GaCl_3$ facilitates the dissociation and possibly the insertion process.

Conclusion

The substituents 2,6-dimethylphenyl (Dmp) and 2,6-diisopropylphenyl (Dipp) impose "medium" substituent steric strain on derivatives of $(RNAsCl)_2$ influencing the relative thermodynamic stability of potential oligomers in favor of the trimers $(RNAsCl)_3$. Extrapolation of observations for phosphazanes to arsazanes demonstrates the general applicability of this new synthetic procedure for the development and diversification of pnictazane chemistry.

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Supporting Information Available: CIF file for the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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