Inorg. Chem. **2005**, *44*, 275–281

A Spirocyclic System Comprising Both Phosphazane and Phosphazene Rings

Philip I. Richards and Alexander Steiner*

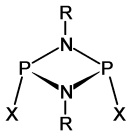
Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, U.K.

Received September 23, 2004

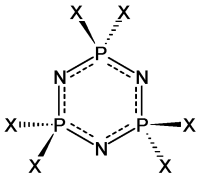
The reaction of hexakis(cyclohexylamino) cyclotriphosphazene $[NP(CyNH)_2]_3$, **1**, with phosphorus trichloride yields $[NP(CyN)_2PCl]_3$, **2**, which contains three four-membered phosphazane rings fused in spirocyclic fashion to a central six-membered phosphazene ring and constitutes the first structurally characterized compound that comprises both phosphazene and phosphazane rings. The peripheral P atoms feature stereoactive lone pairs, and, thus, **2** exists in isomeric C_{3h} and C_s forms. The spirocyclic phosphazene–phosphazane derivative **2** carries three reactive PCl functions in peripheral positions, promising an interesting precursor molecule for the synthesis of extended phosphorus nitrogen structures of high rigidity. Extension of the PN moiety can be achieved by reaction of **2** with a primary amine yielding $[NP(CyN)_2PN(H)^tBu]_3$, **3**, which features a central scaffold of 6 phosphorus and 12 nitrogen centers and aggregates via N–H···P hydrogen bonds in the solid state. On the contrary, the reaction of **1** with $SbCl_3$ undergoes incomplete proton abstraction, resulting in the formation of the tricyclic compound $N_3P_3(CyNH)_4(CyNSbCl_2)_2$, **4**, which contains two four-coordinate Sb centers chelated by N(exo)–N(ring) sites of the phosphazene.

Introduction

Phosphorus nitrogen compounds are renowned for their ability to form a variety of ring and cage structures. The most prominent P−N ring systems are phosph(III)azanes, **I**, featuring single P−N bonds,[1] and phosph(V)azenes, **II**, having multiple P−N bonds.[2] Both systems occur in different ring sizes; however, phosphazanes preferably form four-membered rings, whereas phosphazenes favor six- and eight-membered rings. The ease of introducing a range of substituents X onto phosphorus led to the synthesis of a large number of derivatives. In addition, oxidation of the phosphorus atoms in phosph(III)azanes generates phosph(V)-azanes, in which the P(V) centers carry oxo, thio, seleno, or imino functions.[3] Alternatively, phosph(V)azanes are obtained from the reaction of PCl_5 with a primary amine.[4]



I



II

Both phosphazane and phosphazene ring systems have been applied as scaffolds for multifunctional molecules, such as multidentate ligands.[5,6] Cyclophosphazenes are of exceptional kinetic stability and have been utilized as core units for dendrimers[7] and as nodal ligands in coordination polymers.[8] On the contrary, cyclophosph(III)azanes, depending on the nature of side groups R and X, often undergo interconversion reactions at elevated temperatures, or in the

* Author to whom correspondence should be addressed. E-mail: a.steiner@liv.ac.uk.

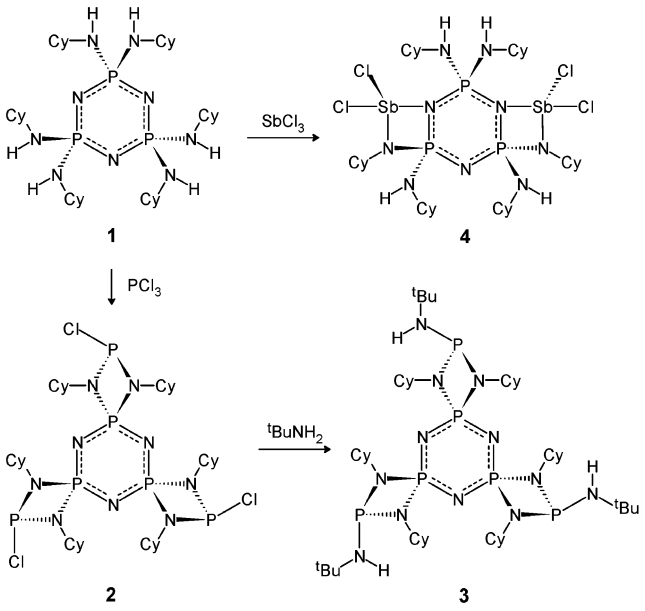
(1) (a) Keat, R. *Top. Curr. Chem.* **1982**, *102*, 89.
(2) (a) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315. (b) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119. (c) Allen, C. W. *Coord. Chem. Rev.* **1994**, *130*, 137. (d) Chandrasekhar, V.; Krishnan, V. *Adv. Inorg. Chem.* **2002**, *53*, 159. (e) Elias, A. J.; Shreeve, J. M. *Adv. Inorg. Chem.* **2001**, *52*, 335.
(3) (a) Briand, G. G.; Chivers, T.; Krahn, M. *Coord. Chem. Rev.* **2002**, *233*, 237. (b) Moser, D. F.; Carrow, C. J.; Stahl, L.; Staples, R. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1246.
(4) Thönnessen, H.; Siedentop, T.; Jones, P. G.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 731 and references therein.
(5) For phosphazane ligands, see: (a) Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203. (b) Schranz, I.; Stahl, L.; Staples, R. J. *Inorg. Chem.* **1998**, *37*, 1493. (c) Grocholl, L.; Schranz, I.; Stahl, L.; Staples, R. J. *Inorg. Chem.* **1998**, *37*, 2496.
(6) For phosphazene ligands, see: (a) Chandrasekhar, V.; Nagendran, S. *Chem. Soc. Rev.* **2001**, *30*, 192. (b) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119. (c) Steiner, A.; Zacchini, S.; Richards, P. I. *Coord. Chem. Rev.* **2002**, *227*, 193.
(7) (a) Caminade, A.-M.; Majoral, J.-P. *Acc. Chem. Res.* **2004**, *37*, 341. (b) Majoral, J.-P.; Caminade, A.-M.; Maraval, V. *Chem. Commun.* **2002**, 2929.
(8) (a) Richards, P. I.; Steiner, A. *Inorg. Chem.* **2004**, *43*, 2810. (b) Richards, P. I.; Benson, M. A.; Steiner, A. *Chem. Commun.* **2003**, 1392.

10.1021/ic048665f CCC: $30.25
Published on Web 12/23/2004

presence of Lewis acids or organometallic reagents, forming polycycles and cage structures.[9] Using halide anions as templates, toroidal phosph(III)azane macrocycles have been synthesized.[10] Although a plethora of cyclic phosphazanes and phosphazenes have been characterized, there are no reports of structurally characterized compounds containing both ring systems.

Recently, we have reported that cyclophosphazenes **II**, which carry six organoamino groups (X = RNH), such as the hexakis(cyclohexylamino) cyclotriphosphazene, **1**, are deprotonated by carbanionic reagents.[11] The metal centers in the resulting multianionic phosphazenates are accommodated in bi- and tridentate coordination sites comprising both ring and exocyclic nitrogen functions (in the following referred to as N(ring) and N(exo), respectively). Herein, we show that analogous reactions with the pnictogen trichlorides PCl_3 and $SbCl_3$ introduce additional P and Sb centers into the PN scaffolds. The reaction with PCl_3 yields the spirocyclic system $[NP(CyN)_2PCl]_3$, **2**, comprising both phosphazene and phosphazane rings, while the reaction with $SbCl_3$ leads to the formation of the tricyclic system $N_3P_3(CyNH)_4(CyNSbCl_2)_2$, **4**, incorporating two antimony atoms. The aminolysis of **2** with *tert*-butylamine yields $[NP(CyN)_2PN(H)^tBu]_3$, **3**. Scheme 1 summarizes the reactions carried out and the products obtained in this study.

Scheme 1



Results and Discussion

The addition of 3 equiv of phosphorus trichloride to a solution of **1**[12] and triethylamine in toluene gives an exothermic reaction leading to the immediate precipitation of triethylammonium chloride. The ^{31}P NMR spectrum of the reaction mixture shows resonances in the regions of δ 25−30 and δ 144−148 (Figure 1). Each region contains one major single peak in conjunction with multiplet signals. The signals observed in the high-field region can be attributed to P(V), and those found in the low-field region are attributed to P(III) centers. Also, the absence of the parent phosphazene **1** is evident from the ^{31}P NMR spectrum. The reaction product was crystallized from toluene/hexane. The IR spectrum indicates the absence of NH functions, but exhibits a strong band at 1199 cm^{-1}, characteristic of stretching frequencies of phosphazene rings.

The X-ray crystal structure determination revealed the formation of the spirocyclic compound $[NP(CyN)_2PCl]_3$, **2** (Figure 2). The crystal lattice also contains one toluene molecule per formula unit. Three P(III)Cl units have replaced the six N-bound protons in **1**, resulting in the formation of three four-membered phosphazane ring systems, which are attached in spirocyclic fashion to the central six-membered phosphazene ring.

Close inspection of the crystal structure reveals that the crystal contains two isomers **2a** and **2b**, which display different orientations of the peripheral PCl units. The core structures comprising P, N, and Cl atoms exhibit C_{3h} symmetry for isomer **2a** and C_s symmetry for isomer **2b**. Both isomers are distributed statistically in the crystal and, thus, are superimposed in the model structure obtained from X-ray structure analysis. Solely the C_{3h} isomer **2a** appears in the initial structure solution. However, upon further refinement, two residual electron density peaks emerge close to one PCl unit of **2a**, indicating the presence of a PCl group of C_s isomer **2b**. The refinement of the occupancy factors

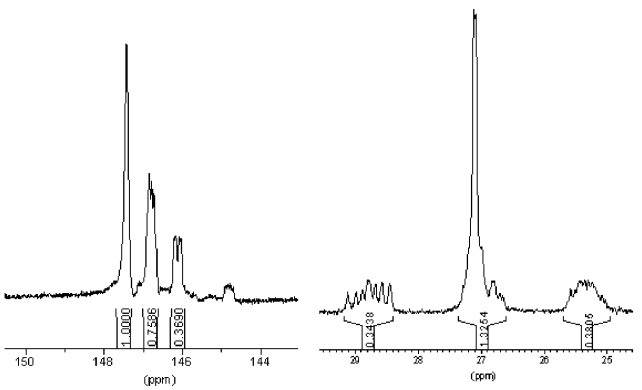


Figure 1. Low- and high-field regions of the ^{31}P NMR spectrum of the reaction of **1** with 3 equiv of PCl_3.

(9) (a) Thompson, M. L.; Tarassoli, A.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1987**, *26*, 684. (b) Tarassoli, A.; Thompson, M. L.; Haltiwanger, R. C.; Hill, G. H.; Norman, A. D. *Inorg. Chem.* **1988**, *27*, 3382. (c) Schranz, I.; Moser, D. F.; Stahl, L.; Staples, R. J. *Inorg. Chem.* **1999**, *38*, 5814. (d) Bashall, A.; Doyle, E. L.; Garcia, F.; Lawson, G. T.; Linton, D. J.; Moncrieff, D.; McPartlin, M.; Woods, A. D.; Wright, D. S. *Chem.-Eur. J.* **2002**, *8*, 5723. (e) Bond, A. D.; Doyle, E. L.; Kidd, S. J.; Woods, A. D.; Wright, D. S. *Chem. Commun.* **2001**, 777. (f) Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Lumsden, M.; MacDonald, C. L. B.; McDonald, R.; Phillips, A. D.; Ragogna, P. J.; Schurko, R. W.; Walsh, D.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2002**, *124*, 14012. (g) Burford, N.; LeBlanc, D. J. *Inorg. Chem.* **1999**, *38*, 2248. (h) Brask, J. K.; Chivers, T.; Krahn, M. L.; Parvez, M. *Inorg. Chem.* **1999**, *38*, 290.

(10) (a) Doyle, E. L.; Riera, L.; Wright, D. S. *Eur. J. Inorg. Chem.* **2003**, 3279. (b) Bashall, A.; Bond, A. D.; Doyle, E. L.; Garcia, F.; Kidd, S.; Lawson, G. T.; Parry, M. C.; McPartlin, M.; Woods, A. D.; Wright, D. S. *Chem.-Eur. J.* **2002**, *8*, 3377.

(11) (a) Lawson, G. T.; Jacob, C.; Steiner, A. *Eur. J. Inorg. Chem.* **1999**, 1881. (b) Lawson, G. T.; Rivals, F.; Tascher, M.; Jacob, C.; Bickley, J. F.; Steiner, A. *Chem. Commun.* **2000**, 341.

(12) Bickley, J. F.; Bonar-Law, R.; Lawson, G. T.; Richards, P. I.; Rivals, F.; Steiner, A.; Zacchini, S. *Dalton Trans.* **2003**, 1235.

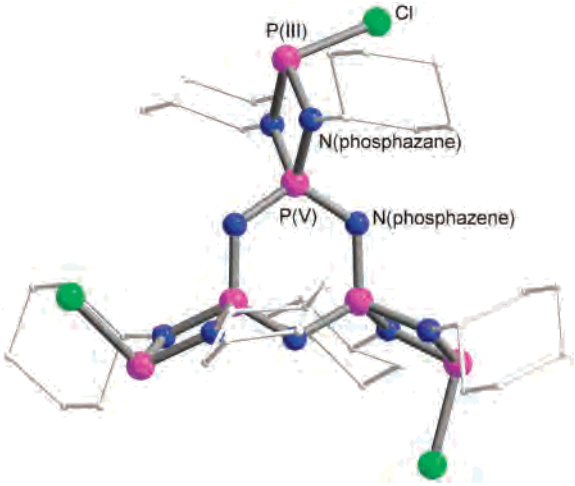
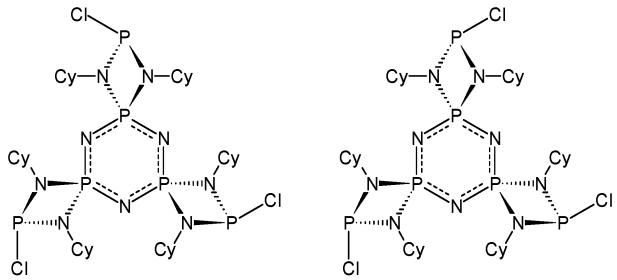


Figure 2. Crystal structure of **2**. Only the major component, isomer **2a**, is shown. Average bond lengths (Å) and angles (deg) in the phosphazene ring, P(V)−N 1.589, N−P(V)−N 115.7, P(V)−N−P(V) 124.1; in the phosphazane rings, P(V)−N 1.674, P(III)−N 1.704, N−P(V)−N 83.8, N−P(III)−N 82.1, P(V)−N−P(III) 97.1; P(III)−Cl 2.146.

of this "disordered" PCl unit displays a **2a**:**2b** ratio of 6:1, which confirms that **2a** is the major component in the crystal. Further atom positions of **2b** could neither be located nor refined, which is probably due to the close proximity of atom positions of both isomers and the low occupancy factor of **2b**.



In the following, only the structural parameters of the major component **2a** are discussed. These compare well with those found in related cyclotriphosphazenes, such as the parent phosphazene **1**,[12] and related cyclodiphosphazanes, for example, the dichloro derivative $(ClPN^tBu)_2$.[13] Both the six-membered phosphazene ring and the three four-membered phosphazane rings are planar. The mean deviation from planarity is only 0.037 Å in the phosphazene ring and ranges from 0.011 to 0.024 Å in the phosphazane rings. The three phosphazane ring planes cut the plane of the central phosphazene ring at approximately right angles (90.2, 90.8, and 91.4 Å, respectively). The phosphazene ring exhibits P−N bonds averaging 1.589 Å, while the P−N bonds in the four-membered phosphazane rings fall into two types. The P(V)−N bonds amount to 1.674 Å, while the P(III)−N bonds are slightly longer, measuring 1.704 Å on average. The P−Cl bonds are 2.146 Å long. The ring angles of the central six-membered phosphazene ring show average values of 115.7° (N−P−N) and 124.1° (P−N−P), respectively. The angles within the four-membered phosphazane rings are considerably sharper measuring 83.8° at P(V), 82.1° at P(III), and 97.1° at N atoms. Although there are many structural similarities to plain phosphazene and phosphazane ring systems, **2a** bears some notable features, if the compound is seen as either a phosphazene or a phosphazane derivative: First, from the phosphazene point of view, the N−P(V)−N angle of the phosphazane ring can also be viewed as the exocyclic X−P−X angle of the central cyclotriphosphazene. As such, it is very acute, measuring only 83.3°. The sharpest exocyclic X−P−X angle of cyclotriphosphazenes described so far are around 90° and occur in metal chelating N(exo)−P−N(exo) units.[14] Second, with regard to phosphazanes, **2** represents a mixed valence phosp(III/V)azane derivative.

The presence of the two stereoisomers **2a** and **2b** is not only apparent in the crystal structure, but also becomes evident when reexamining the ^{31}P NMR spectrum of the reaction mixture, which is displayed in Figure 1. The strong signals at δ 147.6 and 27.1 are caused by the P(III) and P(V) centers of isomer **2a**, which contains two chemically distinct P nuclei. Both signals appear as broadened doublets with coupling constants of around 8 Hz. Isomer **2b** shows a much more complex spectrum because of the distinct chemical environments of its six P-nuclei. The P(III) resonances occur at δ 146.9 and 146.1; the former consists of two overlapping signals. The P(V) resonances appear at δ 28.8, 27.0 (partially masked by the signal of **2a**), and 25.3 and show a complex coupling pattern. It looks as if each P(V) nucleus couples with the other two P(V) nuclei of the central phosphazene ring and the P(III) nucleus located in the associated phosphazane ring system generating a ddd signal pattern as displayed by the set of resonances around δ 28.8. The integrals of signal intensities indicate that both isomers are produced in equal quantities. Although the enrichment of isomer **2a** over **2b** in the crystal suggests that both isomers could be separated by crystallization, we were not successful in obtaining pure isomers by using batch crystallization techniques. Variable-temperature NMR experiments revealed that both isomers do not interconvert in solution at elevated temperature. It is noteworthy that $Li_6[NP(NCy)_2]_3$, the hexalithium complex of **1**,[15] does not react in a similarly smooth manner with 3 equiv of PCl_3, but generates an ill-defined mixture of species. Also, the reaction of **1** with less than 3 equiv of PCl_3 leads to complex product mixtures.

The spirocyclic compound **2** features three reactive chloro functions that facilitate the introduction of a wide variety of peripheral side groups via reaction of **2** with appropriate nucleophiles, such as primary or secondary amines. Treatment of **2** (1:1 mixture of isomers **2a** and **2b** obtained in the reaction described above) with slightly more than 3 equiv of *tert*-butylamine is complete after 2 h of refluxing in

(13) (a) Muir, K. W.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1971**, 1405. (b) Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1975**, 259.

(14) (a) Rivals, F.; Steiner, A. *Eur. J. Inorg. Chem.* **2003**, 3309. (b) Bloy, M.; Diefenbach, U. *Z. Anorg. Allg. Chem.* **2000**, *626*, 885. (c) Veith, M.; Kross, M.; Labarre, J.-F. *J. Mol. Struct.* **1991**, *248*, 345.

(15) Steiner, A.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 636.

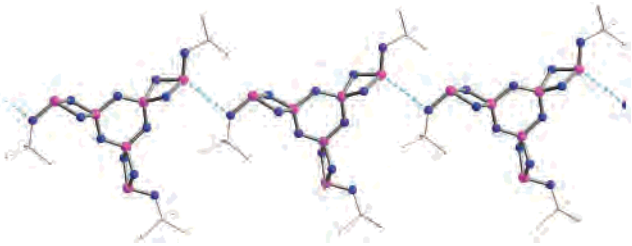


Figure 3. Crystal structure of **3a**. Intermolecular NH···P interactions (dashed lines) result in a supramolecular chain arrangement. Cyclohexyl groups are omitted for clarity.

toluene in the presence of triethylamine. Spectroscopic data of the reaction product suggest full substitution of chloro functions by amino groups, leading to the formation of $[NP(CyN)_2PN(H)^tBu]_3$, **3**. The ^{31}P NMR spectrum of **3** resembles that of **2**, exhibiting distinct regions for signals of P(III) and P(V) centers, which are shifted to higher field as compared to those of **2**. The P(III) region exhibits a broad peak at δ 79.3. In the P(V) region, there are four sets of signals: a sharp peak at δ 18.6 and three pseudo-triplets at δ 21.9, 19.1, and 15.9, respectively. The four signals caused by P(V) centers show an intensity ratio of 3:1:1:1, indicating the presence of equal amounts of both C_{3h} (**3a**) and C_s (**3b**) isomers in solution. The characteristic IR bands at 3134 and 1184 cm^{-1} refer to the N−H stretching frequency and the P−N stretching mode in the phosphazene ring, respectively.

Crystals of **3** were grown from hexane solution and contain one molecule of hexane per formula unit. The crystal structure confirms that full replacement of chlorine atoms by three *tert*-butylamino groups had occurred. The spirocyclic ring structure comprising P and N atoms, which is also part of the parent compound **2**, is retained in the structure of **3**. However, in contrast to the crystals of **2**, which contain both C_{3h} and C_s isomers **2a** and **2b**, the crystal structure of **3** contains only isomer **3a** featuring the C_{3h} symmetrical P_6N_{12} core structure. In the solid state, **3a** displays a crystallographic mirror symmetry. One of the *tert*-butyl groups is *endo* with respect to the plane of the adjacent phosphazane ring leading to an *exo*-H configuration, which in turn enables intermolecular NH···P contacts as shown in Figure 3. The N···P distance of this interaction measures 370 pm, which is in agreement with other NH···P contacts that have been described.[16] Interestingly, several cyclophosphazanes of type **I** carrying exocyclic NH_2 or NH^tBu groups also aggregate via NH···P interactions.[17] The crystal structure of **3a** shows a fair amount of disorder, involving more or less all cyclohexyl and *tert*-butyl groups. In addition, the anisotropic displacement parameters of P and N atoms show a notable elongation orthogonal to the crystallographic mirror plane. This anisotropic behavior indicates some deviation of the molecular mirror plane from the crystallographic mirror plane. A reduction of the space group symmetry from $P2_1/m$ to $P2_1$ did not improve the refinement. While the overall

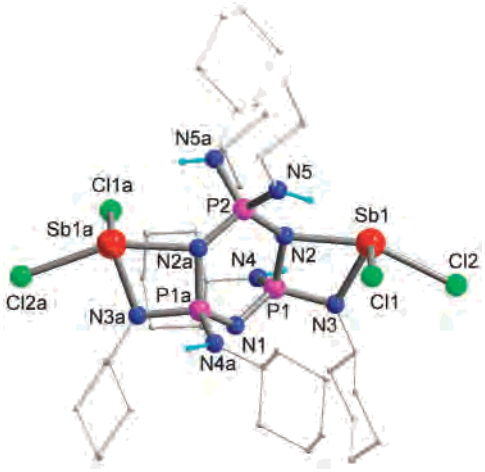


Figure 4. Crystal structure of **4**. Selected bond lengths (Å) and angles (deg): Sb1−N3 2.055(4), Sb1−N2 2.281(4), Sb1−Cl1 2.416(2), Sb1−Cl2 2.557(2), P1−N1 1.582(3), P1−N2 1.656(5), P1−N3 1.651(4), P1−N4 1.608(5), P2−N2 1.609(5), P2−N5 1.628(5); N2−Sb1−N3 67.8(2), Cl1−Sb1−Cl2 90.52(6), N1−P1−N2 113.3(3), N2−P1−N3 94.4(2), N2−P2−N2a 109.5(3), P1−N1−P1a 123.5(4), P1−N2−P2 125.4(3).

connectivity of **3a** is certain, structural parameters, however, should be treated with caution and are not discussed here. A preparative separation of isomers **3a** and **3b** by selective crystallization of **3a** remained unsuccessful, because the crystallization of **3a** is rather slow, not quantitative, and accompanied, if speeded up, by precipitation of a powdery substance containing both isomers.

The addition of 3 equiv of antimony trichloride to **1** in THF in the presence of triethylamine results in the immediate precipitation of Et_3NHCl. After the reaction mixture was stirred for 12 h, the ^{31}P NMR spectrum exhibits an AX_2 spin system containing a triplet at δ 10.0 and a doublet at δ 6.2 with a coupling constant of 44.8 Hz. The same species is obtained when only slightly more than 2 equiv of $SbCl_3$ are applied. The IR spectrum of the isolated solid product exhibits two sharp bands at 3329 and 3298 cm^{-1}, which are attributed to N−H stretching modes, and strong bands at 1109, 1073, and 1038 cm^{-1} referring to stretching modes of the phosphazene ring. The phosphazene bands are considerably red-shifted as compared to the parent phosphazene **1**, indicating a coordination of N(ring) atoms to antimony centers.

The product was crystallized from a mixture of THF and hexane. The crystal structure determination revealed the formation of $N_3P_3(CyNH)_4(CyNSbCl_2)_2$, **4** (Figure 4). Two $SbCl_2$ units are accommodated in N(ring)−P−N(exo) chelates at opposite sides and faces of the P_3N_3 ring, resulting in a tricyclic system comprising two four-membered SbNPN rings, which are attached to the central six-membered phosphazene ring. Contrasting the full deprotonation of **1** by PCl_3, only two exocyclic amino groups were deprotonated by $SbCl_3$. The resulting antimony complex **4** exhibits crystallographic C_2 symmetry. The Sb−N(exo) bonds measure 2.055(4) Å and are markedly shorter than the Sb−N(ring) bonds, which amount to 2.281(4) Å. This indicates a mainly covalent character of the Sb−N(exo) bonds and a dative character of the N(ring) atoms to the antimony centers.

(16) Andrieu, J.; Baldoli, C.; Maiorana, S.; Poli, R.; Richard, P. *Eur. J. Org. Chem.* **1999**, 3095.
(17) (a) Woods, A. D.; McPartlin, M. *Dalton Trans.* **2004**, 90. (b) Beswick, M. A.; Elvidge, B. R.; Feeder, N.; Kidd, S. J.; Wright, D. S. *Chem. Commun.* **2001**, 379.

In comparison, covalent Sb−N bonds as in tris(mesitylamino)stibane[18] are around 2.05 Å. Trivalent antimony centers are able to act as Lewis acids and form dative bonds with donor centers. Dative Sb−N bonds are observed in a number of compounds and show a wide range of Sb−N distances varying from 2.2 to 2.6 Å.[19]

The central six-membered phosphazene ring deviates from planarity, exhibiting a slight twist along the crystallographic 2-fold axis. The mean deviation from planarity is 0.144 Å. P−N bond lengths within the phosphazene ring vary as a result of the partial deprotonation of exocyclic amino groups and the coordination of N(ring) atoms to Sb centers. The P−N(ring) bond lengths are 1.582(3), 1.609(5), and 1.656(5) Å. The longer bond is associated with the P−N(ring) bond that is also part of the four-membered SbNPN ring, while the shortest P−N(ring) bond involves the N(ring) center, which does not coordinate to Sb centers. There is also a variation of P−N(exo) bond lengths measuring 1.608(5), 1.628(5), and 1.651(4) Å. The latter and somewhat longer bond is associated with the two deprotonated N(exo) sites that coordinate to antimony centers. This is in contrast to the variation of P−N(exo) bonds in lithium complexes containing partially deprotonated phosphazenate ligands. Those exhibit short P−N(exo) bonds at the deprotonated, lithium-coordinating N-sites and noticeably longer P−N bonds involving the NH groups. The difference of P−N(exo) bond lengths in antimony and lithium complexes can be ascribed to the different bonding modes of the Li−N(exo) and Sb−N(exo) interactions. In the case of the ionic Li−N(exo) interaction, the exocyclic nitrogen atom holds a substantial negative charge, which enhances the electrostatic interaction with the adjacent P(V) center and, thus, shortens the P−N(exo) bond. On the contrary, the covalent character of the Sb−N(exo) bond in **4** leaves less negative charge on the N(exo) atom. The N−P−N angles in **4** are also affected by the coordination of N-sites to antimony centers. The most acute N−P−N angle in **4** measures 94.4(2)° and is displayed by the N(exo)−P−N(ring) chelate that is part of the four-membered SbNPN ring. The N(ring)−P−N(ring) angles are 109.5(3)° and 113.3(3)°, and P−N(ring)−P angles are 123.5(4)° and 125.4(3)°, the latter involving N(ring) sites that coordinate to Sb centers.

The environment of the antimony center describes a distorted octahedral geometry featuring the stereoactive lone pair and a weak intermolecular Sb···Cl interaction in addition to the four covalent interactions to chlorine and nitrogen atoms. Two neighboring coordination sites are occupied by the chelate comprising the N(exo) and the N(ring) atom. The corresponding N−Sb−N angle is 67.8(2)°. The two chlorine atoms also occupy neighboring positions on the coordination sphere of the antimony center and display a Cl−Sb−Cl angle of 90.52(6)°. The Sb−Cl bonds measure 2.416(2) and 2.557(2) Å, respectively. The chlorine atom associated with the longer Sb−Cl bond is located in the trans position to the N(ring) site. The deviation from linearity of the Cl−Sb−N(ring) angle measuring 156.8(1)° is a consequence of the acute N−Sb−N angle and the spatial requirements of the stereoactive lone pair, which is located in the trans position to the N(exo) coordination. Both Sb−Cl bonds are slightly longer than in $SbCl_3$,[20] but are in agreement with those found in four-coordinate antimony(III) complexes.[21] The two remaining octahedral sites around the Sb center are occupied by the stereoactive lone pair and by a long-range interaction toward a chlorine atom of a neighboring molecule (Sb···Cl 3.409(2) Å). These long-range intermolecular interactions are common for compounds featuring four-coordinate Sb(III) centers.[21] In addition, all NH functions and chlorine atoms in **4** participate in either intra- or intermolecular hydrogen bonding, resulting in a supramolecular chain structure, which is displayed in Figure 5. The N···Cl distances within NH···Cl interactions are 3.363(5) and 3.364(5) Å, respectively.

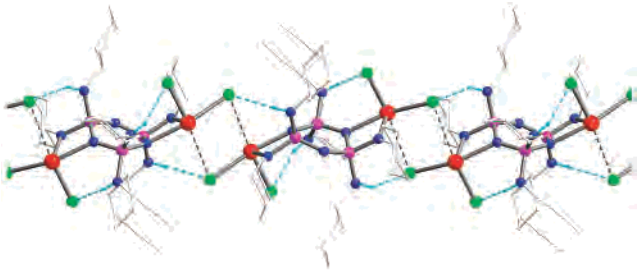


Figure 5. Supramolecular chain structure of **4** in the solid state. Hydrogen bonds are drawn as turquoise dashed lines, and weak intermolecular Sb···Cl contacts are drawn as gray dashed lines.

It is noteworthy that the reaction of **1** with 3 equiv of $SbCl_3$ under prolonged refluxing in THF leads to the formation of further products as monitored by ^{31}P NMR spectroscopy. The AX_2 signal due to **4** disappeared, and three complex signals of more or less equal intensity emerged at δ 14.5, 11.6, and 3.8. This suggests that deprotonation of additional NH functions occurred, but attempts to obtain pure products from this reaction remained fruitless. However, the absence of a dominant single peak rules out the presence of spirocyclic derivatives analogous to **2**. The different reaction pathways of **1** with PCl_3 and $SbCl_3$ can be rationalized by the enhanced acceptor properties of the Sb(III) center. Furthermore, the N(ring) sites of **1** are far more basic than the amino side groups[8b] and, thus, might play a significant role in the reaction of **1** with electrophiles. Scheme 2 displays a possible reaction mechanism. The initial stage on the reaction pathway could consist of an adduct complex, in which the N(ring) site interacts with ECl_3 (E = P, Sb).[22] The close proximity of the NH functions to the activated ECl_3 molecule leads to E−N(exo) bond formation under elimination of HCl. In the case of E = Sb, the initial adduct eliminates 1 equiv of HCl,

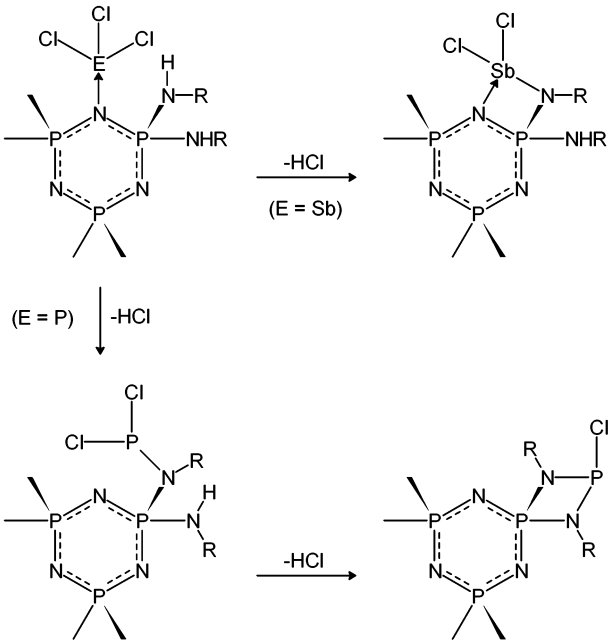
(18) Burford, N.; MacDonald, C. L. B.; Robertson, K. N.; Cameron, T. S. *Inorg. Chem.* **1996**, *35*, 4013.

(19) See, for example: (a) Carmalt, C. J.; Cowley, A. H.; Culp, R. D.; Jones, R. A.; Kamepalli, S.; Norman, N. C. *Inorg. Chem.* **1997**, *36*, 2770. (b) Opris, L. M.; Silvestru, A.; Silvestru, C.; Breunig, H. J.; Lork, E. *Dalton Trans.* **2003**, 4367. (c) van den Ancker, T. R.; Andrews, P. C.; King, S. J.; McGrady, J. E.; Raston, C. L.; Roberts, B. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *607*, 213.

(20) Lipka, A. *Acta Crystallogr.* **1979**, *B35*, 3020.

(21) (a) Ergezinger, C.; Weller, F.; Dehnicke, K. *Z. Naturforsch.* **1988**, *B43*, 1119. (b) Ensinger, U.; Schwarz, W.; Schmidt, A. *Z. Naturforsch.* **1982**, *B37*, 1584.

Scheme 2



leading to the stable four-coordinate Sb center, which is chelated by a N(ring)−N(exo) unit. The formation of a second Sb−N(exo) bond, accompanied by elimination of HCl, is inhibited, because this would strain and eventually break the Sb−N(ring) bond generating an unsaturated three-coordinate Sb(III) center. On the other hand, the initial interaction of PCl_3 with the N(ring) site eases the departure of one chloride ion, and the phosphorus center forms, presumably in two successive steps, two covalent P−N(exo) bonds with neighboring amino groups under elimination of 2 equiv of HCl, which results in a stable trivalent P(III) center. In contrast, the cyclophosphazane R′NHP(RN)$_2$PNHR′, which carries exocyclic R′NH groups at its P centers, is deprotonated twice by 1 equiv of PCl_3 and $SbCl_3$, repsectively.[23] In the resulting products, the PCl unit bridges the two exocyclic N centers, whereas, in addition, the SbCl unit interacts weakly with one N(ring) atom in the solid state.

Conclusion

The reaction of the cyclophosphazene [NP(CyNH)$_2$]$_3$, **1**, featuring six amino side groups, with PCl_3 yields the spirocyclic system [NP(CyN)$_2$PCl]$_3$, **2**, which constitutes the first structurally characterized compound that comprises both phosphazene and phosphazane rings. The corresponding reaction of **1** with $SbCl_3$ undergoes incomplete proton abstraction, resulting in the formation of the tricyclic compound **4** containing two four-coordinate Sb centers, which are chelated by N(exo)−N(ring) sites. We made the enhanced acceptor properties of Sb(III) over P(III) responsible for this behavior. The spirocyclic phosphazene−phosphazane derivative **2** carries three reactive PCl functions in peripheral positions. This promises an interesting precursor molecule for the synthesis of extended phosphorus nitrogen structures of high rigidity. Extension of the PN moiety can be achieved by reaction of **2** with a primary amine yielding [NP(CyN)$_2$PN(H)^{t}Bu]$_3$, **3**, that comprises a central scaffold of 6 phosphorus and 12 nitrogen centers. In addition, there is a wide range of feasible reactions that could be applied to both **2** and **3** to extend the PN scaffold further. Likely routes involve the oxidation of the peripheral P(III) centers by either Kirsanov- or Staudinger-type reactions. Again, the resulting products would bear reactive sites facilitating the iterative assembly of rigid phosphorus nitrogen polycycles.

Experimental Section

General Procedures. All experiments were performed under inert gas atmosphere using standard Schlenk glassware and a glovebox. Solvents were dried over sodium (toluene) and potassium (hexane, THF, Et_3N), respectively. PCl_3 was distilled prior to use. The phosphazene precursor **1** was prepared as described previously.[12] FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer in Nujol between CsI plates. NMR spectra were recorded on a Bruker AMX 400 spectrometer at room temperature using $SiMe_4$ (for ^{1}H and ^{13}C) and 85% H_3PO_4 (for ^{31}P) as external standards.

Preparation of 2. First, 1.00 g (1.38 mmol) of **1** was dissolved in 20 mL of toluene. The solution was cooled to −78 °C. To this solution were added 4.6 mL (33 mmol) of Et_3N and 0.38 mL (4.28 mmol) of PCl_3. A cloudy precipitate formed immediately. The straw-yellow solution was allowed to warm to room temperature and was stirred for 12 h. The precipitate was filtered off leaving a straw-yellow solution. All volatiles were removed under reduced pressure giving a yellow solid. Single crystals were collected from a toluene/hexane solution at 5 °C and lose lattice solvent under vacuum. Yield 1.01 g (72%).

Mp: 286 °C. ^{1}H NMR (400.13 MHz, d_8-toluene, 25 °C, TMS): δ = 0.8−2.1 (br, cyclohexyl groups). ^{13}C{^{1}H} NMR (100.62 MHz, d_8-toluene): δ = 24.3, 33.3, 51.6. ^{31}P{^{1}H} NMR (161.97 MHz, toluene): δ = 147.6 (d, 3P, P(III), **2a**), 146.9 (m, 2P, P(III), **2b**), 146.1 (m, 1P, P(III), **2b**), 28.8 (m, 1P, P(V), **2b**), 27.1 (d, 3P, P(V), **2a**), 27.0 (m, 1P, P(V), **2b**), and 25.3 (m, 1P, P(V), **2b**). IR (Nujol): ν(cm^1) = 1258, 1199 (P−N stretch), 1144, 1085, 1050, 939, 833. Anal. Calcd for $C_{36}H_{66}Cl_3N_9P_6$: C, 47.14; H, 7.25; N, 13.74. Found: C, 47.45; H, 7.60; N, 13.54.

Preparation of 3. To a stirred solution of 1.00 g (0.99 mmol) of **2** in 40 mL of toluene and 0.83 mL (5.94 mmol) of triethylamine was added 0.63 mL (5.94 mmol) of *tert*-butylamine at room temperature. The formation of a white precipitate indicated the onset of the reaction. The solution was heated to reflux for 2 h and then cooled prior to filtration. The solvent and excess amines were removed under reduced pressure to yield the product as a straw-yellow solid. Single crystals were collected from a hexane solution at −20 °C and lose lattice solvent under vacuum. Yield 0.86 g (84%).

Mp: 148 °C. ^{1}H NMR (400.13 MHz, d_8-toluene): δ = 0.8−2.1 (br, cyclohexyl and *tert*-butyl groups). ^{13}C{^{1}H} NMR (100.62 MHz, d_8-toluene): δ = 24.8, 25.0, 31.6, 51.1. ^{31}P{^{1}H} NMR (161.97 MHz, toluene): δ = 79.3 (br, 6P, P(III), **3a** and **3b**), 21.9 (m, 1P, P(V), **3b**), 19.1 (m, 1P, P(V), **3b**), 18.6 (s, 3P, P(V), **3a**), and 15.9

(22) Structurally characterized amine adducts of both phosphorus and antimony trihalides have been reported: (a) The adduct Et_3N-PBr_3 displays a dative N−P bond of 1.98 Å and one substantially elongated P−Br bond of 2.87 Å, see: Müller, G.; Brand, J.; Jetter, E. *Z. Naturforsch.* **2001**, *B56*, 1163. (b) For the adduct pyridine−$SbCl_3$, see: Lipka, A. *Z. Naturforsch.* **2001**, *B38*, 341.

(23) (a) Schranz, I.; Grocholl, L. P.; Stahl, L.; Staples, R. J.; Johnson, A. *Inorg. Chem.* **2000**, *39*, 3037. (b) Moser, D. F.; Schranz, I.; Stahl, L.; Staples, R. J. *J. Chem. Soc., Dalton Trans.* **1999**, 751.

Table 1. Crystallographic Data of **2**·C_7H_8, **3**·C_6H_{14}, and **4**

	2·C_7H_8	**3a**·C_6H_{14}	**4**
chem formula	$C_{43}H_{74}Cl_3N_9P_6$	$C_{54}H_{110}N_{12}P_6$	$C_{36}H_{70}Cl_4N_9P_3Sb_2$
fw	1009.28	1113.36	1107.22
space group	$P2_1/n$	$P2_1/m$	$C2/c$
a, Å	16.132(4)	11.4414(6)	20.723(3)
b, Å	16.755(4)	24.2507(14)	12.771(2)
c, Å	19.004(4)	12.2069(6)	19.949(3)
β, deg	91.729(4)	108.6010(10)	114.263(3)
V, Å^3	5135(2)	3210.0(3)	4813.2(13)
Z	4	2	4
ρ_{calc}, g cm^{-1}	1.306	1.152	1.528
μ, mm^{-1}	0.406	0.211	1.481
$R(F)$ [$I > 2\sigma(I)$]	0.083	0.093	0.049
wR2(F^2) (all data)	0.230	0.273	0.120

(m, 1P, P(V), **3b**). IR (Nujol): ν(cm^{-1}) = 3134 (N−H stretch), 1255, 1184 (P−N stretch), 1091, 1012, 930, 817, 688. Anal. Calcd for $C_{48}H_{96}N_{12}P_6$: C, 56.13; H, 9.42; N, 16.36. Found: C, 56.23; H, 9.60; N, 16.02.

Preparation of 4. First, 1.00 g (1.38 mmol) of **1** was dissolved in 20 mL of THF. The solution was cooled to −78 °C. To this solution were added 2.31 mL (16 mmol) of Et_3N and 0.95 g (4.14 mmol) of $SbCl_3$ in 10 mL of THF. A colorless precipitate formed slowly. The solution was allowed to warm to room temperature and was stirred for 12 h. The precipitate was filtered off leaving a clear solution. All volatiles were removed under reduced pressure giving the product as a white solid. Single crystals were obtained from a THF/hexane solution at 25 °C. Yield 2.08 g (68%).

Mp: 205 °C (decomp.). ^{1}H NMR (400.13 MHz, d_8-toluene): δ = 0.8−2.2 (br, cyclohexyl groups). ^{13}C{^{1}H} NMR (100.62 MHz, d_8-toluene): δ = 24.7, 32.8, 51.4. ^{31}P{^{1}H} NMR (161.97 MHz, toluene): δ = 9.96 (t, 1P, $^2J_{pp}$ = 44.8 Hz), 6.20 (d, 2P, $^2J_{pp}$ = 44.8 Hz). IR (Nujol): ν(cm^{-1}) = 3329 (N−H stretch), 3298 (N−H stretch), 1262, 1199, 1109 (P−N stretch), 1073 (P−N stretch), 1038 (P−N stretch), 939, 912, 841, 821, 798, 778. Anal. Calcd for $C_{36}H_{70}Cl_4N_9P_3Sb_2$: C, 39.05; H, 6.37; N, 11.38. Found: C, 38.92; H, 6.31; N, 11.02.

X-ray Crystallography. Crystallographic data were recorded on a Bruker Smart Apex diffractometer using Mo Kα radiation (λ = 0.71073 Å) at T = 150 K. Structures were solved by Direct Methods and refined by full-matrix least squares against F^2 using all data (SHELXTL). All non-H atoms were refined anisotropically with the exception of disordered atoms. H-atoms were fixed in calculated positions at parent C and N atoms, respectively. Disordered atoms were split on two positions (unless stated otherwise) and refined using similar distance and similar U restraints (Table 1). This included one PCl unit, two cyclohexyl groups (one of which is disordered over three positions), the toluene molecule (also disordered over three positions) in **2**·toluene, and two cyclohexyl and three *tert*-butyl groups in **3a**·C_6H_{14}. A semiempirical absorption correction based upon equivalent and redundant reflections was applied to the data of **4** (min./max. transmission: 0.775).

Acknowledgment. We thank the EPSRC for financial support.

Supporting Information Available: X-ray crystallographic data in CIF format for **2**·C_7H_8, **3a**·C_6H_{14}, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048665F