Chemistry of Boratophosphazenes: Synthesis of Borazine – Phosphazene Hybrid Cations, and New Inorganic Heterocycles by Skeletal Substitution Reactions

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Abstract: The structural characterization of the boratophosphazene $N(PCl_2NMe)_2BCl_2$ (**1**) is reported and reveals a distorted structure in which the boron atom is bent out of the plane of the other ring atoms (0.39(1) Å) and the axial B – Cl bond is highly elongated. Halide abstraction with Lewis acids, $AlCl_3$ and $GaCl_3$, yielded the first well-characterized examples of borazine – phosphazene hybrid cations $[N(PCl_2NMe)_2BCl]^+$, ([**2**][$AlCl_4$], and [**2**][$GaCl_4$] respectively), which were fully characterized spectroscopically and crystallographically. Halide abstraction with BCl_3 also yielded the borazine hybrid cation [**2**][BCl_4], which was characterized crystallographically; however, in solution there was evidence for coordination of the anion. The structures of the ions $[\mathbf{2}]^+$ show the presence of planar rings with B – N bond lengths (ca. 1.44 Å) characteristic for borazines and P – N bond lengths (ca. 1.56 Å) typical for phosphazenes. Attempts to coordinate amines (D), such as NEt_3 and quinuclidine to [**2**][$GaCl_4$], resulted in the regeneration of **1** and the formation of Lewis-base adducts $D\cdot GaCl_3$. Evidence for the formation of a product involving amine coordination to the boron atom of [**2**][$GaCl_4$] was found with quinuclidine. Variation of the anion present was attempted by use of Ag^+ salts with $[BF_4]^-$ and $[OSO_2CF_3]^-$ anions. Reaction of **1** with 2 equiv of $Ag[OSO_2CF_3]$ afforded $N(PCl_2NMe)_2B(OSO_2CF_3)_2$ (**7**). Similarly, reaction with $Ag[BF_4]$ produced $N(PCl_2NMe)_2BF_2$ (**8**). The reaction of **1** with silver(I) salts containing even less coordinating anions (e.g., $[AsF_6]^-$ and $[SbF_6]^-$) resulted in the discovery of a new type of reaction for boron-containing heterocycles. Thus the As and Sb atoms were found to replace boron in a skeletal substitution reaction forming novel arsenic(V) [$N(PCl_2NMe)_2AsF_4$, (**9**)] and antimony(V) heterophosphazenes [$N(PCl_2NMe)_2SbF_4$ (**10a**) and $N(PCl_2NMe)_2SbF_3Cl$ (**10b**)]. In solution, a complex fluxional behavior was observed for **9** by variable-temperature ^{19}F and ^{31}P NMR spectroscopy. With the discovery of the skeletal substitution reactions, questions were raised with regard to the mechanism of formation of **8** from the reaction of $Ag[BF_4]$ and **1**. Thus, ^{10}B-labeled **1** was prepared and the reaction with $Ag[BF_4]$ was found to proceed with substantial skeletal substitution from ^{10}B and ^{11}B NMR analysis and mass spectrometry.

Keywords: aromaticity · borazines · heterocycles · phosphazenes · structure elucidation

Introduction

Inorganic heterocycles have attracted considerable recent attention, because of the interesting questions they pose with respect to structure and bonding, and their function as precursors to inorganic polymers by ring-opening polymerization (ROP), and to ceramics by pyrolysis.[1–3] The ring skeleton present in many inorganic heterocycles has been found to be quite robust and stable, and halogenated derivatives undergo facile side-group substitution reactions without degradation of the ring structure.[4] The cyclic phosphazene trimer $(NPCl_2)_3$ is one of the most well-studied ring systems that is known to undergo ROP.[5] Also, several heterophosphazenes containing, for example, carbon, sulfur(IV), sulfur(VI), and metals have been reported to undergo facile thermal ROP reactions to yield high molecular weight polymers.[6–9] In the case of the polymers containing sulfur(VI) atoms, poly(thionylphosphazenes), these have also been shown to have potential applications in the aerospace industry as gas-permeable matrices for pressure-sensing applications.[10, 11]

With this in mind we have chosen to investigate boron-containing heterophosphazenes, which represent an underdeveloped area of inorganic chemistry and may provide access to new inorganic polymers through ROP. In fact, very

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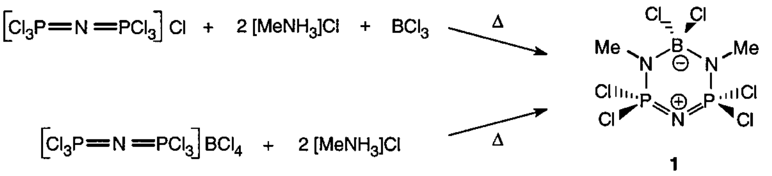
few examples of rings constructed from boron, nitrogen, and phosphorus atoms are known,[12] which is surprising since borazines and phosphazenes represent two of the most well-studied textbook classes of inorganic ring systems. The first report of a N_3P_2B ring, R$\overline{\mathrm{BNP(Ph_2)NP(Ph_2)N}}$H, was made in 1966 by Schmulbach et al. and the synthesis involved a [5+1] cyclocondensation reaction between $[H_2NPh_2P{=}N{=}PPh_2NH_2]Cl$ and $RBCl_2$ (R = Ph or Cl). However characterization was limited to infrared and UV spectroscopy, and elemental analysis.[13] The same researchers also briefly reported salts of a borazine–phosphazene cation of type [Cl$\overline{\mathrm{BNHP(Ph_2)NP(Ph_2)N}}$H]$BCl_4$, but these materials were also only partially characterized. Due to our interest in B–N–P systems as precursors to inorganic polymers, and the fact that cyclic phosphazenes containing alkyl or aryl side groups do not polymerize,[14] we chose to focus our studies on the perhalogenated boratophosphazene $N(PCl_2NMe)_2BCl_2$ (**1**). This compound was originally synthesized by Becke-Goehring from the reaction between $[Cl_3P{=}N{=}PCl_3]Cl$, $(MeNH_3)Cl$, and BCl_3;[15] however, improved yields were reported by Binder, through the reaction of $[Cl_3P{=}N{=}PCl_3]BCl_4$ with $(MeNH_3)Cl$ (Scheme 1).[16]



Scheme 1. Reaction scheme for the formation of **1**.

This paper, as a follow-up to our communications,[17] reports a detailed study of the reactivity of **1** with a wide variety of halide acceptors. These types of study may also ultimately provide insight into polymerization behavior, since ROP reactions of phosphazene-based heterocycles are proposed to involve a cationic mechanism.[18]

Results and Discussion

Synthesis and structure of the boratophosphazene 1: When first studied, compound **1** was proposed to have a zwitterionic structure with a formal negative charge at boron and a formal positive charge at the nitrogen atom on the opposite side of the ring, although initial studies in polar solvents (ie. CH_3CN) suggested that partial heterolytic dissociation of a B–Cl bond may take place.[15] However, through our studies of **1** by NMR spectroscopy in CD_3CN, $CDCl_3$, or CD_2Cl_2 solution no evidence of dissociation was detected, with four lines in the ^{31}P NMR spectrum in $CDCl_3$ ($\delta = 28.2$, $^2J_{BP} = 15$ Hz) and, even more convincingly, a sharp 1:2:1 triplet in the ^{11}B NMR spectrum at $\delta = 5.4$ ($^2J_{BP} = 15$ Hz). Because of our interest in the bonding in **1** and the almost complete lack of structural information for boron–nitrogen–phosphorus rings, we characterized the boratophosphazene by X-ray crystallography.

Single crystals were obtained from cooling a concentrated solution of **1** in dichloromethane to −30 °C. Two views of the molecular structure of **1** are shown in Figure 1. Remarkably, the ring was found to deviate significantly from planarity, and the boron atom was positioned 0.39(1) Å away from the best plane of the other five ring atoms. Of particular interest is that the P–N bonds flanking N(3) are shorter (av 1.547(5) Å) than those involving the methyl-substituted nitrogen atoms N(1) and N(2) (av 1.593(5) Å). This suggests a greater degree of π bonding in the case of the former bonds and is consistent with the proposed Lewis structure showing a formal positive charge on N(3). For comparison, the phosphorus–nitrogen bonds in $[Cl_3P{=}N{=}PCl_3]^+$ are 1.51–1.56 Å long,[19] and a typical P–N single bond is 1.78 Å.[20] Significantly, however, the P(1)–N(1) and P(2)–N(2) bonds (av 1.593(5) Å) are similar in length to the P–N bonds in $(NPCl_2)_3$ (1.58 Å),[21] which suggests that the lone pairs on N(1) and N(2) are involved in the π bonding to the phosphorus atoms of the P(1)-N(3)-P(2) fragment. Further evidence for π bonding is provided by the trigonal planar rather than pyramidal geometry of N(1) and N(2). The B–N bonds have lengths (av 1.533(5) Å) indicative of predominantly single-bond

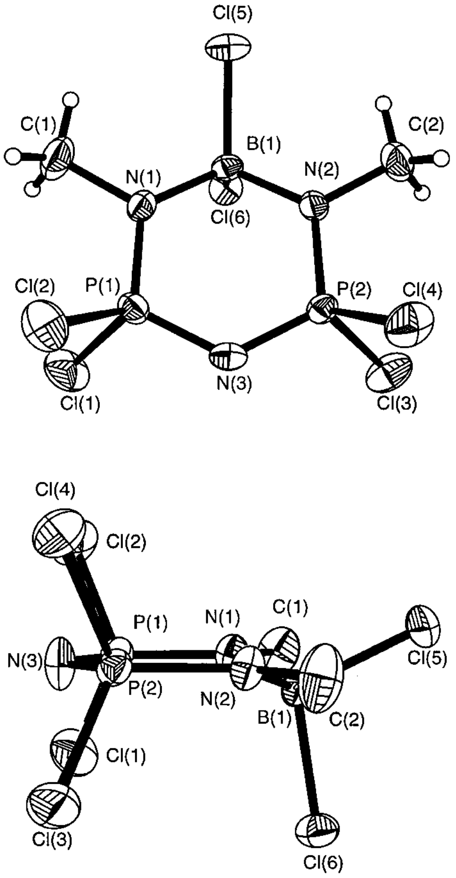
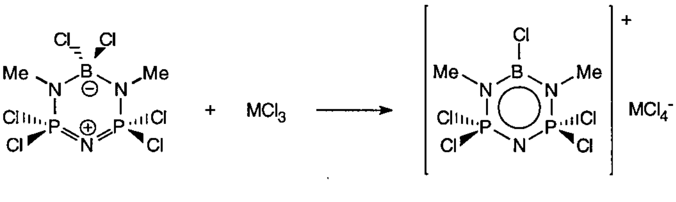


Figure 1. Molecular structure of **1** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: B(1)–N(1) 1.536(6), N(1)–P(1) 1.583(4), P(1)–N(3) 1.551(4), N(3)–P(2) 1.544(4), P(2)–N(2) 1.602(4), N(2)–B(1) 1.531(5), B(1)–Cl(5) 1.847(5), B(1)–Cl(6) 1.903(4); N(1)-B(1)-N(2) 113.9(3), B(1)-N(2)-P(2) 122.2(3), N(2)-P(2)-N(3) 113.7(2), P(2)-N(3)-P(1) 125.7(3), N(3)-P(1)-N(1) 113.9(2), P(1)-N(1)-B(1) 122.3(3).

character as the typical range for B–N single bonds is 1.58–1.59 Å, whereas B=N double bonds are generally about 1.41 Å.[22] Nevertheless, the B–N bonds are still markedly shorter than a typical single bond (for $(Cl_2BNMe_2)_2$, the B–N length is 1.591(10) Å),[23] suggesting the possibility of some degree of π character in the skeletal N-B-N moiety. This postulate is supported by a careful consideration of the environment about the boron atom B(1). Remarkably, the two boron–chlorine bonds differ significantly, with the B(1)–Cl(5) bond lying approximately in the best plane of the NP_2N_3 ring and 1.847(5) Å long, which is comparable to that found in cyclic chloroborane–amine adducts such as the dimeric species $(Cl_2BNMe_2)_2$ [1.830(10) Å].[23] In contrast, the B(1)–Cl(6) bond is approximately perpendicular to the best plane of the six-membered ring and is markedly elongated to 1.903(4) Å. Together with the significant shortening of the skeletal B–N bonds, this elongation suggests that Cl(6) is close to heterolytic dissociation, which would generate a borazine-like planar environment at B(1).

Synthesis and spectroscopic characterization of borazine–phosphazene hybrid cations: In view of the long B–Cl(6) bond observed in **1** and our interest in investigating the reactivity of this relatively unexplored class of ring system, we decided to attempt halide abstraction using a variety of Lewis acids. Addition of $AlCl_3$ in CH_2Cl_2 to a solution of **1** in the same solvent gave no color change. However, analysis of the product by ^{11}B NMR spectroscopy showed that **1** [$\delta = 5.4$ (t)] was completely consumed and that a new product [**2**][$AlCl_4$] with a broad singlet resonance at $\delta = 29.6$ in $CDCl_3$ was formed (Scheme 2). This downfield shift and the broadening of the ^{11}B NMR resonance for [**2**][$AlCl_4$] suggests the presence of a planar rather than tetrahedral environment at boron. Significantly, the ^{11}B NMR chemical shift for $[\mathbf{2}]^+$ is similar to that for the borazine $(ClBNMe)_3$ ($\delta = 31.2$).[24] In addition, the ^{31}P resonance of [**2**][$AlCl_4$] ($\delta = 34.8$) is shifted downfield from that of **1** ($\delta = 28.2$) and now consists of a single broad resonance as compared with the four-line pattern observed in **1**. Analysis of the product by ^1H NMR ($\delta = 3.32$) and ^{13}C NMR ($\delta = 35.5$) revealed slight downfield shifts from those of **1** (δ $^1H = 3.23$; δ $^{13}C = 33.3$). Similarly, [**2**][$GaCl_4$] can be prepared by reaction of a $GaCl_3$ solution with **1** in dichloromethane. This compound has similar spectroscopic properties to [**2**][$AlCl_4$] with a broad ^{11}B NMR resonance in $CDCl_3$ at $\delta = 30.2$ and a ^{31}P NMR resonance at $\delta = 35.0$. Similar downfield shifts with respect to **1** were observed in the ^1H and ^{13}C NMR spectra of [**2**][$GaCl_4$] (δ $^1H = 3.36$; δ $^{13}C = 35.7$).



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2[AlCl₄]
2[GaCl₄]

Scheme 2. Reaction scheme for the formation of [**2**][$AlCl_4$] and [**2**][$GaCl_4$].

X-ray structural studies of borazine–phosphazene hybrid cations $[\mathbf{2}]^+$: In order to probe the structure and bonding in this new class of compound, the products of the reactions were studied by X-ray crystallography. Crystals of [**2**][$AlCl_4$] and [**2**][$GaCl_4$] suitable for X-ray diffraction were obtained by either cooling a CH_2Cl_2/hexanes solution of the compound or by slow solvent evaporation. Borazine–phosphazene hybrids [**2**][$AlCl_4$] and [**2**][$GaCl_4$] are isostructural; front and side views of [**2**][$AlCl_4$] are shown in Figure 2 and summaries of important structural features of these compounds are listed in Table 1. The structures were consistent with the spectroscopic data, and confirmed that the chlorine atom attached to boron in **1** had successfully been abstracted to yield a boron–nitrogen–phosphorus cation with tetrachloroaluminate or -gallate as the counterion. No significant interactions between the cation and anion were observed, with the closest B···Cl(6) contacts in [**2**][$AlCl_4$] and [**2**][$GaCl_4$] being 3.223(3) Å and 3.223(3) Å, respectively, and the closest N···Cl contacts being 3.381 Å (N(2)···Cl(9) in [**2**][$AlCl_4$]) and 3.980(3) Å (N(1)···Cl(9) in [**2**][$GaCl_4$]). The rings deviate only slightly from planarity with the largest deviation being at N(1) in both [**2**][$AlCl_4$] (0.22(1) Å) and [**2**][$GaCl_4$] (0.11(1) Å).

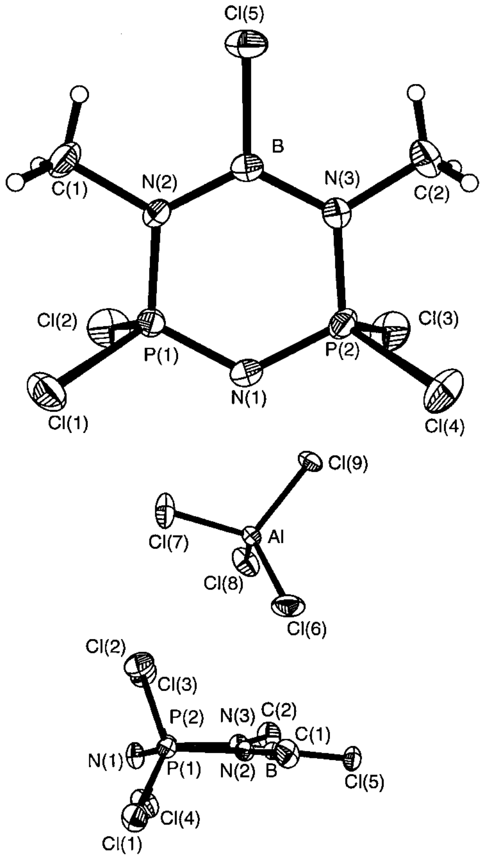


Figure 2. Molecular structure of [**2**][$AlCl_4$] with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: B–N(2) 1.446(4), N(2)–P(1) 1.626(2), P(1)–N(1) 1.557(2), N(3)–P(2) 1.627(2), N(3)–B 1.444(4), B–Cl(5) 1.752(5); N(2)-B-N(3) 124.0(2), B-N(3)-P(2) 121.8(2), N(3)-P(2)-N(1) 112.39(12), P(2)-N(1)-P(1) 125.3(2), N(1)-P(1)-N(2) 112.26(12), P(1)-N(2)-B 121.6(2).

Table 1. Selected structural features of BN_3P_2 heterocycles.

	1	[**2**][$AlCl_4$]	[**2**][$GaCl_4$]	[**2**][BCl_4]	**7**	**8**
$[B-N]_{av}$	1.533(6)	1.445(5)	1.429(10)	1.448(7)	1.509(11)	1.552(5)
$[P-N(Me)]_{av}$	1.593(5)	1.626(3)	1.624(6)	1.623(5)	1.590(7)	1.584(3)
$[P-N(P)]_{av}$	1.547(5)	1.558(4)	1.551(8)	1.563(7)	1.548(7)	1.556(4)
[N-B-N]	113.9(3)	124.0(2)	124.2(6)	124.6(4)	116.4(6)	112.9(2)
$[B-N-P]_{av}$	122.2(4)	121.7(3)	121.8(6)	121.5(4)	125.3(6)	126.0(3)
$[P-N-P]_{av}$	125.7(3)	125.3(2)	125.4(4)	125.8(3)	126.3(4)	124.5(2)
[N-P-N]	113.8(3)	112.3(2)	112.1(4)	112.8(3)	113.3(5)	114.5(2)
deviation from planarity[a]	0.39(1)	0.22(1)	0.11(1)	0.13(1)	0.02(1)	0.17(1)

[a] maximum distance that one atom is from the plane of the other five ring atoms (for **1** [B(1)], for [**2**][BCl_4] [N(3)], for [**2**][$AlCl_4$] [N(1)], for [**2**][$GaCl_4$] [N(1)], for **7** [P(1′) molecule 2], for **8** [N(1)]).

One striking feature of the molecular structures of [**2**][$AlCl_4$] and [**2**][$GaCl_4$] is the boron–nitrogen distance, which has shortened dramatically from **1** (av 1.533(6) Å) to an average value of 1.445(5) Å for [**2**][$AlCl_4$] and 1.429(10) Å for [**2**][$GaCl_4$]. This indicates an increased degree of π bonding in the cations and, furthermore, the B–N bond lengths are similar to those found in the borazines (1.43 Å).[22] Accompanying this dramatic shortening of the B–N bonds is a significant widening of the N-B-N bond angle from 113.9(3)° in **1** to 124.0(2)° in [**2**][$AlCl_4$] and 124.2(6)° in [**2**][$GaCl_4$]. This is consistent with a planar borazine-like environment. In addition, the B–Cl(5) bond lengths for [**2**][$AlCl_4$] and [**2**][$GaCl_4$], 1.752(3) and 1.747(8) Å, are substantially shorter than the shortest B–Cl bond in **1** (1.847(5) Å) and are similar to the bond lengths in BCl_3 (ca. 1.75 Å).[25] They are also consistent with some degree of π donation from chlorine to boron and the sp^3–sp^2 hybridization change.

The P–N(Me) bonds are longer (av 1.626(5) Å for [**2**][$AlCl_4$], 1.624(6) Å for [**2**][$GaCl_4$]) than the analogous bonds in **1** (av 1.593(5) Å) and are also much longer than the P–N(P) bonds (av 1.558(4) Å for [**2**][$AlCl_4$], 1.551(8) Å for [**2**][$GaCl_4$]), reflecting increased double-bond character in the P-N-P fragment. The slight elongation of the P–N(Me) bonds in $[\mathbf{2}]^+$ is possibly a reflection of the increase in π donation from the lone electron pair on nitrogen into the empty 2p orbital of boron, subsequently leaving less possibility for a similar donation into the empty 3d orbital on phosphorus; however, they are shorter than the longest P–N bonds in $(Cl_3PNMe)_2$ (1.769(7) Å).[26] The P–N(P) bonds in $[\mathbf{2}]^+$ are similar to those of **1** (1.547(5) Å), reflecting the lack of change in electronic structure at this end of the molecule. Interestingly, these bonds are similar in length to those found in the cyclic phosphazene $(NPCl_2)_3$.[21]

Synthesis, characterization, and solution behavior of [2][BCl_4]: In order to extend the range of salts containing the borazine–phosphazene hybrid cation $[\mathbf{2}]^+$, an attempt was made to prepare the compound [**2**][BCl_4] by halide abstraction from **1** with BCl_3. Thus, an equimolar reaction between BCl_3 and **1** in dichloromethane solution was carried out and, after solvent removal in vacuo, this yielded a colorless solid. Examination of the product by X-ray crystallography showed that the solid-state structure was the borazine–phosphazene hybrid [**2**][BCl_4]. The molecular structure of [**2**][BCl_4] is shown in Figure 3; in contrast to the structures of [**2**][$AlCl_4$] and [**2**][$GaCl_4$], this compound was found to crystallize in the monoclinic lattice (space group *Cc*) rather than the triclinic lattice (space group $P\bar{1}$). Nevertheless, the structural features of this molecule are similar to those found for [**2**][$AlCl_4$] and [**2**][$GaCl_4$], with a planar ring [largest deviation: 0.13(1) Å at N(3)] and no close contacts between cation and anion were observed in the crystal, with the closest B(1)⋯Cl(9) distance being 3.103(5) Å, and the closest N(2)⋯Cl(9) distance 3.222(4) Å. Interestingly, these are significantly less than the closest contacts in [**2**][$AlCl_4$] and [**2**][$GaCl_4$] reflecting a possible weak interaction between the anion and cation in [**2**][BCl_4]. The environment at boron also exhibits similarities with that of borazine, with an average B–N bond length of 1.448(7) Å + and an N-B-N bond angle of 124.6(4)°.

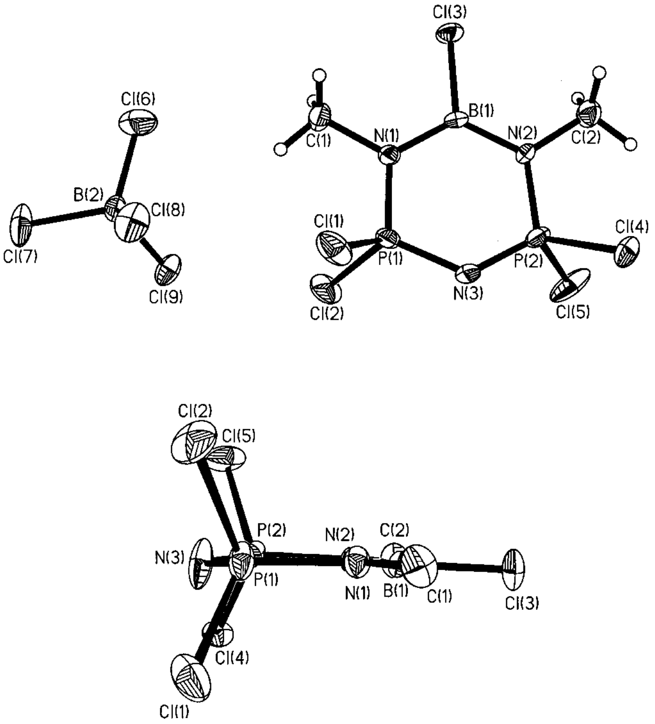
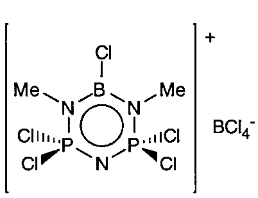
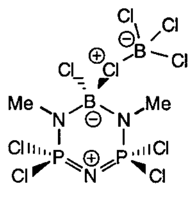


Figure 3. Molecular structure of [**2**][BCl_4] with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: B(1)–N(1) 1.462(6), N(1)–P(1) 1.618(4), P(1)–N(3) 1.579(6), N(3)–P(2) 1.548(6), P(2)–N(2) 1.628(4), N(2)–B(1) 1.434(7), B(1)–Cl(3) 1.743(5); N(1)-B(1)-N(2) 124.6(4), B(1)-N(2)-P(2) 121.7(3), N(2)-P(2)-N(3) 113.0(2), P(2)-N(3)-P(1) 125.8(3), N(3)-P(1)-N(1) 112.6(2), P(1)-N(1)-B(1) 121.4(4).

Analysis of the crystals redissolved in $CDCl_3$ by ^{31}P NMR spectroscopy showed a singlet resonance at $\delta = 28.4$, and the ^{11}B NMR spectrum showed two sharp resonances at $\delta = 6.5$ and 40.2.[27] Interestingly, this is more consistent with the presence of a species with a structure such as **3**, or even **1** (δ $^{31}P = 28.2$; δ $^{11}B = 5.4$) and BCl_3 (δ $^{11}B = 46.7$). Binder also studied the reaction of **1** with BCl_3 in 1977, and reported the NMR spectra for the reaction mixture in 1,2-dichloroethane solution (δ $^{31}P = 26.0$; δ $^{11}B = 6.0$). He thus considered three



2[BCl$_4$]



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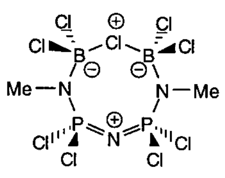

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possible solution structures; namely, [**2**][BCl$_4$], an adduct (**3**) of BCl$_3$ and **1** (i.e. **3**), and the unexpected ring-expansion product **4**.[28] Although only **4** made spectroscopic sense because of the observation of a single ^{11}B NMR resonance, it was concluded that **3** was the most likely product.[29]

Because of our differing observations, we have studied the reaction of **1** with BCl$_3$ in more detail. An NMR-scale reaction between **1** and a slight excess of BCl$_3$ (20%) in CD$_2$Cl$_2$ was performed, and analysis by ^{11}B NMR spectroscopy showed a sharp signal at $\delta = 12.3$ and a broad resonance at $\delta = 29.9$, which is consistent with that previously observed for [**2**]$^+$. The ^{31}P NMR spectrum exhibited a singlet resonance at $\delta = 34.7$, which is consistent with [**2**]$^+$, and a resonance at $\delta = 30.0$, which lies closer to that for **1** than [**2**]$^+$, and is consistent with the presence of adduct **3**. In addition, a broad resonance is observed in the ^{31}P NMR spectrum between the resonances at $\delta = 30.0$ and 34.7; this suggests that an exchange process may be occurring. A ^{10}B labeling experiment was carried out to determine whether **4** is formed and to provide insight into the possible exchange process in solution. Reaction between **1** (99% ^{10}B) and 1 equiv BCl$_3$ was undertaken in CD$_2$Cl$_2$ solution, and the ^{31}P NMR spectrum showed the formation of a new product at $\delta = 32.9$ that was shifted slightly downfield from the starting material **1** (99% ^{10}B), which has a single resonance at $\delta = 27.9$ in CD$_2$Cl$_2$. This is intermediate between the chemical shifts observed in the unlabeled experiment, which utilized excess BCl$_3$, and is presumably a result of the 1:1 stoichiometry. The ^{10}B and ^{11}B NMR spectra are shown in Figure 4, and the ^{10}B NMR spectrum shows that the sharp resonance for starting material **1** (99% ^{10}B) at $\delta = 5.7$ was almost completely consumed and two new resonances were observed, with a sharp singlet at $\delta = 10.6$ and a very broad resonance at $\delta = 24.6$. In contrast, the ^{11}B NMR spectrum of the reaction mixture, after about 2 h, showed only one dominant sharp resonance at $\delta = 10.4$, and a very small broad peak at $\delta = 26.0$ was observed. This shows that there is no appreciable insertion of BCl$_3$ into the ring to form **4**, which would result in exchange of the ^{10}B atoms in **1** with the natural abundance boron atoms in BCl$_3$; thus the same ratios of the peaks in both the ^{11}B and ^{10}B NMR spectra would be observed. Furthermore, no evidence for free BCl$_3$ in solution was observed in either experiment; for this species a downfield resonance in both the ^{10}B and ^{11}B NMR spectra (ca. $\delta = 46$) would be expected.

Thus, it can be concluded that [**2**][BCl$_4$] and **3** are present in equilibrium in the reaction mixture and each can be observed by ^{31}P NMR in a reaction with excess BCl$_3$. This equilibrium can be shifted toward [**2**][BCl$_4$] or **3** depending on the ratio used (and perhaps concentration), but the mechanism does not involve insertion into the ring to form **4**. Upon redissolution of the crystals obtained from the reaction, the major species in solution was likely to be a dissociated product **1** + BCl$_3$ and not **3**. Additionally, the crystals of [**2**][BCl$_4$] were found to spontaneously lose BCl$_3$ over time regenerating **1**. This is similar to the behavior reported by Schmulbach for [N(PPh$_2$NH)$_2$BCl]BCl$_4$, which was claimed to lose BCl$_3$ under vacuum according to elemental analysis and infrared spectroscopy.[13]

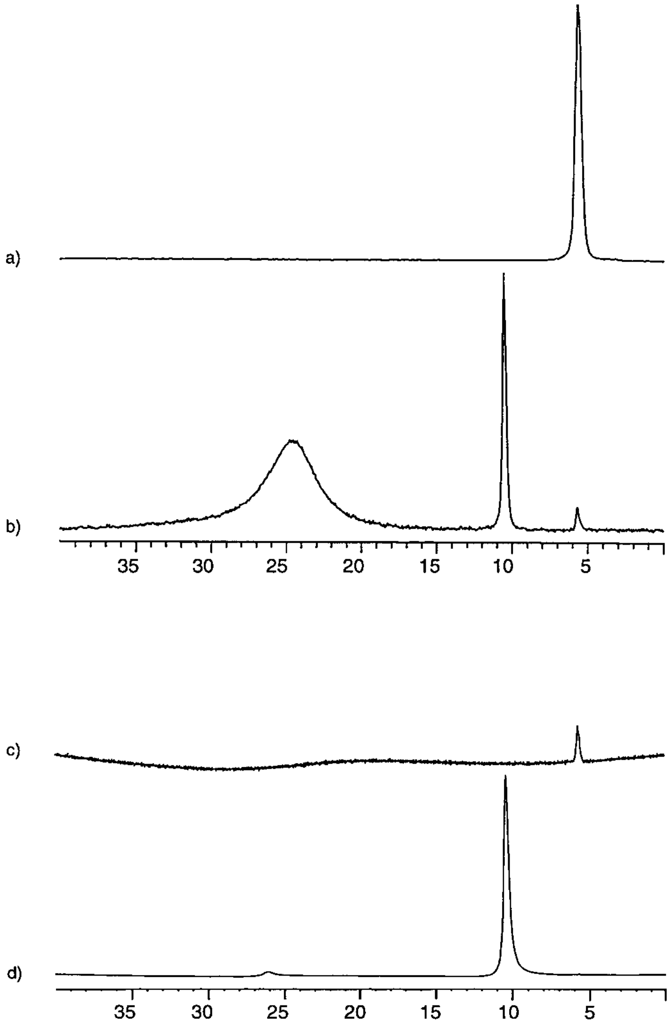
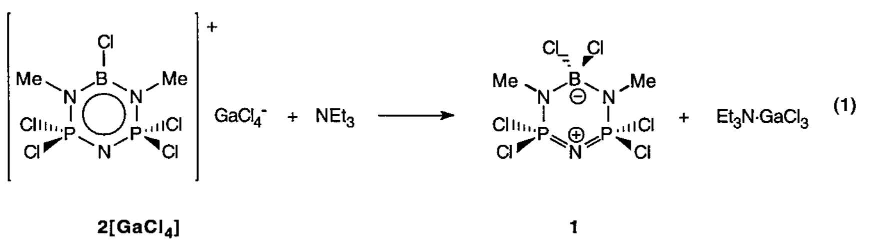
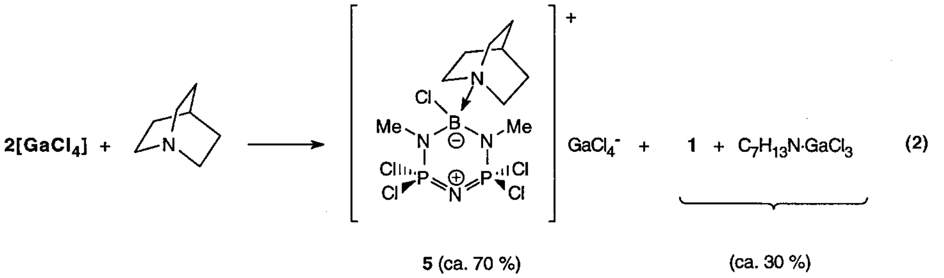


Figure 4. ^{10}B labeling study of the reaction between **1** (99% ^{10}B) and BCl$_3$ in CD$_2$Cl$_2$. a) ^{10}B NMR spectrum of **1** (99% ^{10}B); b) ^{10}B NMR spectrum after the addition of BCl$_3$; c) ^{11}B NMR spectrum of **1** (99% ^{10}B); d) ^{11}B NMR spectrum after the addition of BCl$_3$.

Reactivity of borazine–phosphazene hybrid cation [2]$^+$: To understand the electrophilic reactivity of [**2**]$^+$ and to investigate the potential of back coordination of chlorine to the borazine–phosphazene hybrid observed in solution for [**2**][BCl$_4$] with other anions, we explored the reaction of the borazine–phosphazene cation [**2**][GaCl$_4$] with two amine



2[GaCl$_4$] 1 (1)



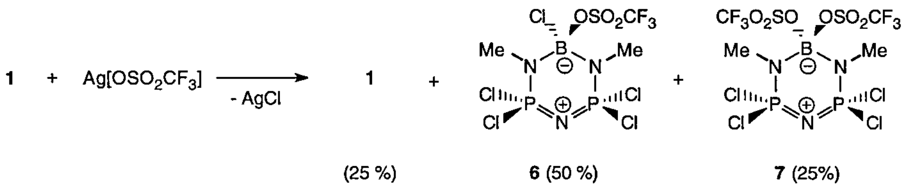
5 (ca. 70 %) (ca. 30 %) (2)

nucleophiles. Addition of a dichloromethane solution of NEt$_3$ to a solution of [**2**][GaCl$_4$] in the same solvent showed a single ^{31}P NMR four-line resonance at $\delta = 28.2$ and an ^{11}B NMR resonance at $\delta = 5.6$. This suggested the formation of **1** [Equation (1)] as one of the products and implied formation of Et$_3$N·GaCl$_3$, rather than the expected formation of the adduct of NEt$_3$ with the borazine–phosphazene hybrid cation. This was confirmed by an X-ray analysis of the two types of crystals formed in the reaction, which showed formation of the boratophosphazene **1** and the Et$_3$N·GaCl$_3$ adduct.[30]

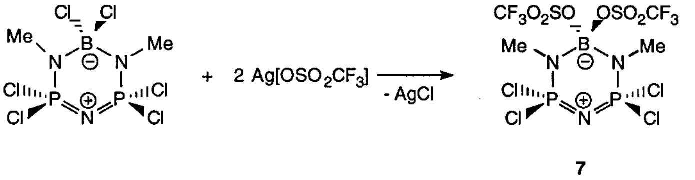
When an alternative base, quinuclidine, was added to a solution of [**2**][GaCl$_4$] in CDCl$_3$ [Equation (2)], the formation of two new quartets was observed in the ^{31}P NMR spectrum, one at $\delta = 28.0$ (ca. 30 %) and the other at $\delta = 36.2$ (ca. 70 %), and [**2**][GaCl$_4$] ($\delta = 35.0$) was completely consumed. This suggested the competing formation of both the adduct (**5**) of quinuclidine with [**2**][GaCl$_4$] and halide transfer of a chlorine from the anion [GaCl$_4$]$^-$ to the borazine–phosphazene hybrid cation. The ^{11}B NMR spectrum exhibited two overlapping resonances, the major peak being at $\delta = 6.5$ for **5** and a shoulder at $\delta = 5.9$ assigned to **1**. Attempts to separate the products by fractional recrystallization resulted in an intensity increase for the species with a ^{31}P NMR resonance at $\delta = 36.3$ with respect to **1**; however, the crystals obtained were not suitable for X-ray diffraction.

Attempted generation of borazine–phosphazene hybrid cations [2]$^+$ with [OSO$_2$CF$_3$]$^-$ and [BF$_4$]$^-$ counterions: The base-induced transfer of chlorine in the tetrachlorogallate anion to the boron atom in [**2**]$^+$ prompted us to explore the synthesis of [**2**]$^+$ with alternative anions in which this type of halide transfer would not occur. We chose Ag$^+$ as the halide acceptor with a series of counterions. Thus, a solution of the boratophosphazene **1** in CH$_2$Cl$_2$ was added to a slurry of Ag[OSO$_2$CF$_3$] (1:1) in CH$_2$Cl$_2$, and after stirring for several hours the colorless solution was decanted from a white precipitate. The ^{31}P NMR spectrum exhibited three sets of pseudoquartets ($\delta = 28.0$, 29.1, and 30.6) in approximately 1:2:1 ratio, rather than the broad singlet around $\delta = 35$ that would be expected for the borazine–phosphazene hybrid cation. Nevertheless, these can be assigned to three different species with quaternary boron atoms, **1**, **6**, and **7** [Equation (3)], and these assignments were supported by the ^{11}B NMR spectrum, which exhibited three sharp resonances at high field ($\delta = 1.6$, 4.3, and 5.5) consistent with four-coordinate boron. In addition, there was no indication of the formation of the borazine–phosphazene hybrid cation [**2**]$^+$. This can be explained by the strong bonding between boron and oxygen, and suggests that the triflate anion is more coordinating than the Group 13 tetrahalide anions.

The reaction of **1** with two equivalents of Ag[OSO$_2$CF$_3$] or the mixture of **1**, **6**, and **7** with a further equivalent of Ag[OSO$_2$CF$_3$] produced bis(triflato)boratophosphazene **7** quantitatively [Equation (4)] as observed by ^{31}P NMR ($\delta = 30.6$). The ^{11}B NMR spectrum of **7** in CDCl$_3$ consisted of a single sharp resonance at $\delta = 1.6$. The presence of the triflate anion was confirmed by ^{19}F NMR spectroscopy in CDCl$_3$, which showed a singlet resonance at $\delta = -77.4$ that is similar to that observed for triflic acid ($\delta = -78.48$),[31] and the ^{13}C NMR spectrum showed a quartet resonance at $\delta = 118.3$ assigned to the CF$_3$ group in addition to the methyl resonance at $\delta = 31.2$.

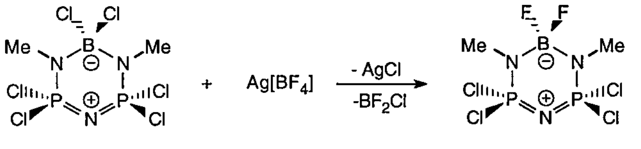


(25 %) 6 (50 %) 7 (25%) (3)



7 (4)

This prompted us to treat the boratophosphazene **1** with Ag[BF_4] with the view that the $[BF_4]^-$ anion might be less coordinating than the triflate anion. When a solution of the boratophosphazene was added to a slurry of Ag[BF_4] in CH_2Cl_2, the immediate elimination of a gas (which fumed in air) was observed. After several hours of vigorous stirring, the colorless solution was decanted from the white precipitate and ^{31}P NMR analysis of the reaction mixture in CH_2Cl_2 showed the quantitative formation of a new product with a quartet resonance at $\delta = 29.0$. This was not consistent with the formation of a borazine–phosphazene hybrid cation, but was consistent with halide transfer of fluorine and formation of a four-coordinate boron center. This new product **8** [Equation (5)] was isolated as a white solid in vacuo, and



1 **8** (5)

spectroscopic analysis of this solid in $CDCl_3$ by ^{31}P NMR gave a quartet resonance at $\delta = 28.3$, a single resonance in the ^{11}B NMR at $\delta = 2.8$, and a single peak at $\delta = -147.5$ in the ^{19}F NMR spectrum. Thus, it was postulated that BF_nCl_{3-n} had been eliminated as a highly reactive gas that fumes in air, and fluoride had thus been back-donated to boron. The nature of the cyclic product was confirmed by an X-ray crystallographic analysis. Compound **8** has previously been obtained by Binder from the reaction of SbF_3 with **1**.[28]

X-ray crystal structures of boratophosphazenes 7 and 8: In order to confirm the structures of **7** and **8**, and to provide further structural information on the bonding present in boratophosphazenes, crystallographic analyses were undertaken. The most striking feature of the molecular structures of **7** and **8** (Figures 5 and 6) is the planarity of the ring, with the largest deviation from the plane of the other five ring atoms being at P(1′) in **7** and N(1) in **8** (0.02(1) Å and 0.17(1) Å, respectively). This was very surprising, because it was thought that the nonplanar structure in **1** was due in part to the fact that the maximum coordination number (four) for boron had been achieved and thus the lone pair of electrons on the nitrogen atoms were localized, causing distortion at those sites. There are no distortions in the bonding of the boron atom, with the average B–O bond lengths in **7** being 1.524(10) Å, and the B–F bonds in **8** are only slightly different (B–F(1) 1.409(4) Å; B–F(2) 1.384(4) Å) and do not show the axial/equatorial behavior that the chlorine atoms in **1** exhibit. Other than the planarity of the rings, the other features of the structures are quite unremarkable, with B–N and P–N bond lengths, and major bond angles similar to **1**.

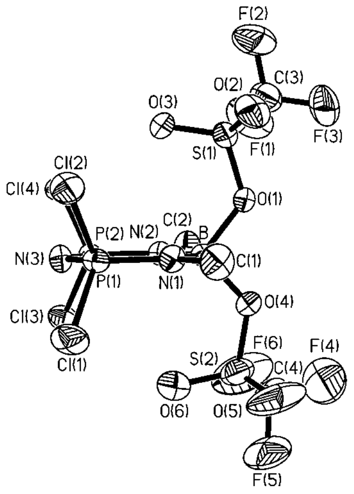


Figure 5. Molecular structure of **7** (molecule 1) with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: B–N(1) 1.512(9), N(1)–P(1) 1.598(5), P(1)–N(3) 1.549(5), N(3)–P(2) 1.548(5), P(2)–N(2) 1.582(5), N(2)–B 1.517(9), B–O(1) 1.530(8), B–O(4) 1.505(8); N(1)-B-N(2) 116.3(5), B-N(2)-P(2) 125.4(4), N(2)-P(2)-N(3) 113.7(2), P(2)-N(3)-P(1) 126.1(3), N(3)-P(1)-N(1) 113.3(2), P(1)-N(1)-B 125.2(4); Molecule 2: B′–N(1′) 1.509(9), N(1′)–P(1′) 1.588(5), P(1′)–N(3′) 1.538(5), N(3′)–P(2′) 1.555(5), P(2′)–N(2′) 1.590(5), N(2′)–B′ 1.499(9), B′–O(1′) 1.528(8), B′–O(4′) 1.534(8); N(1′)-B′-N(2′) 116.6(5), B′-N(2′)-P(2′) 125.2(4), N(2′)-P(2′)-N(3′) 113.2(3), P(2′)-N(3′)-P(1′) 126.5(3), N(3′)-P(1′)-N(1′) 113.0(3), P(1′)-N(1′)-B′ 125.4(4).

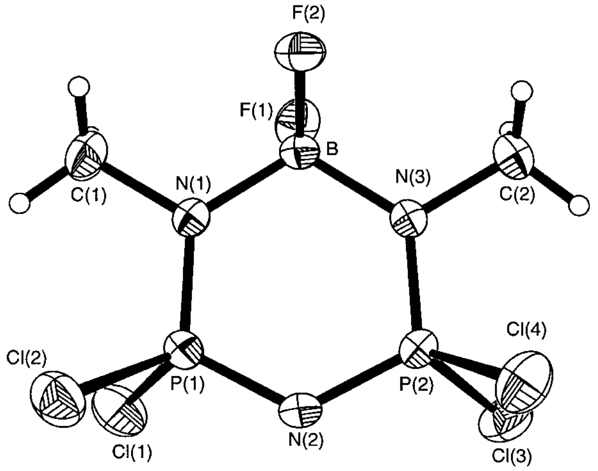
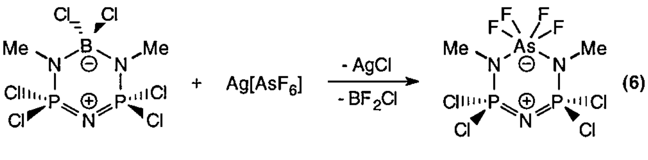


Figure 6. Molecular structure of **8** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: B–N(1) 1.551(4), N(1)–P(1) 1.582(2), P(1)–N(2) 1.554(3), N(2)–P(2) 1.558(3), P(2)–N(3) 1.586(2), N(3)–B 1.552(4), B–F(1) 1.409(4), B–F(2) 1.384(4); N(1)-B-N(3) 112.9(2), B-N(3)-P(2) 126.4(2), N(3)-P(2)-N(2) 114.36(14), P(2)-N(2)-P(1) 124.5(2), N(2)-P(1)-N(1) 114.64(14), P(1)-N(1)-B 125.6(2).

Attempted synthesis of $[2]^+$ with $[AsF_6]^-$ and $[SbF_6]^-$ counterions: discovery of skeletal substitution reactions.

1) Reaction of 1 with Ag[AsF₆]: The reactivity of the triflate and tetrafluoroborate anions with $[2]^+$ prompted us to explore the possibility of preparing this species with alternative, less reactive anions. When a solution of **1** was added to Ag[AsF_6] in CH_2Cl_2, the immediate formation of a fine white precipitate of AgCl was observed. After 12 h a slight pressure buildup was detected. The solution was then decanted, and the solvent removed to yield a white crystalline solid. The product was analyzed by ^{31}P NMR in $CDCl_3$, which showed the presence of a dominant singlet at $\delta = 30.6$. This resonance was not consistent with the formation of the analogue of $[2]^+$ with $[AsF_6]^-$ as counterion (for [**2**][$GaCl_4$], $\delta(^{31}P, CDCl_3) = 35.0$). Remarkably, no nonvolatile boron-containing species were detected by ^{11}B NMR. Colorless crystals were obtained by slow evaporation of solvent from a solution of the product in dichloromethane/hexanes (1:1). A crystal was analyzed by X-ray diffraction, which surprisingly showed the product of the reaction to be the arsenic(v) heterophosphazene **9** [Equation (6)].



(6)

1 **9**

One striking feature of the molecular structure of **9** (Figure 7) is that the compound is in the boat conformation, with As and N(1) removed substantially from the plane of the other four ring atoms by 0.85(1) Å and 0.33(1) Å, respectively. Unlike in **1**, in which one B–Cl bond is highly elongated, all As–F bonds in **9** are equal (1.724(2)–1.735(3) Å) and are longer than the As(v)–F bonds in $[AsF_6]^-$ (1.68 Å).[32] The P–N bonds flanking N(1) [P(1)–N(1) and P(2)–N(1)] are shorter (av 1.558(6) Å) than those involving the methyl-substituted nitrogen atoms N(2) and N(3) (P(1)–N(2) and P(2)–N(3); av 1.592(5) Å). This suggests a greater degree of π bonding in the former bonds and is consistent with the presence of a positive charge on N(1) analogous to the situation in **1** (av 1.547(4) Å). Due to the lack of structural data on As(v)–N-containing heterocycles, a detailed analysis of the arsenic(v) environment in **9** is difficult. However, the As–N bond lengths (av 1.905(6) Å) are similar to the longest bonds found in the cyclodiars(v)azane $[\{(CF_3)_2ClAsNSiMe_3\}_2]$ (As–N = 1.933(7) Å)[33] and are longer than the As–N multiple bonds in the arsazene $[\{NAsPh_2\}_3]$ (av 1.758(4) Å).[34] For comparison, a typical As–N single bond length has been calculated to be 1.87 Å from Pauling's covalent single-bond radii. Mass spectrometric analysis of **9** supports the X-ray structure with the identification of a molecular ion $[M^+]$ with the expected isotope pattern.

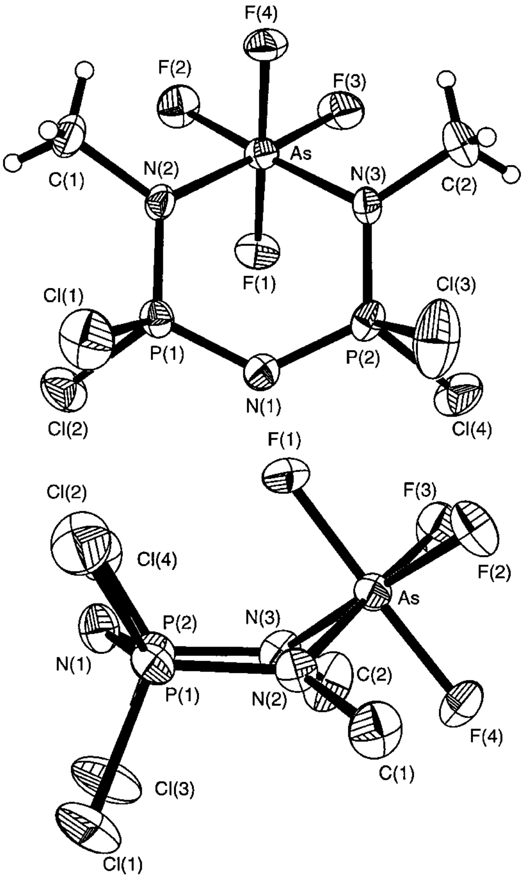


Figure 7. Molecular structure of **9** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: As-N(2) 1.907(6), N(2)-P(1) 1.589(4), P(1)-N(1) 1.555(4), N(1)-P(2) 1.562(4), P(2)-N(3) 1.595(4), N(3)-As 1.903(4), As-F(1) 1.735(3), As-F(2) 1.731(3), As-F(3) 1.724(2), As-F(4) 1.727(3); N(2)-As-N(3) 93.3(2), As-N(3)-P(2) 121.5(2), N(3)-P(2)-N(1) 114.6(2), P(2)-N(1)-P(1) 124.8(2), N(1)-P(1)-N(2) 114.5(2), P(1)-N(2)-As 121.3(2).

At room temperature, the ^{19}F NMR spectrum of a pure sample of **9** in $CDCl_3$ or CD_2Cl_2 exhibited only very broad resonances between $\delta = -35$ and -45, and $\delta = -50$ and -60. The broadness of the ^{19}F resonances observed at 39 °C (Figure 8) suggested that $\mathbf{9}_{boat}$ was fluxional in solution, which was not unexpected since similar six-membered rings formed by chelating ligands to octahedral metal centers are known to

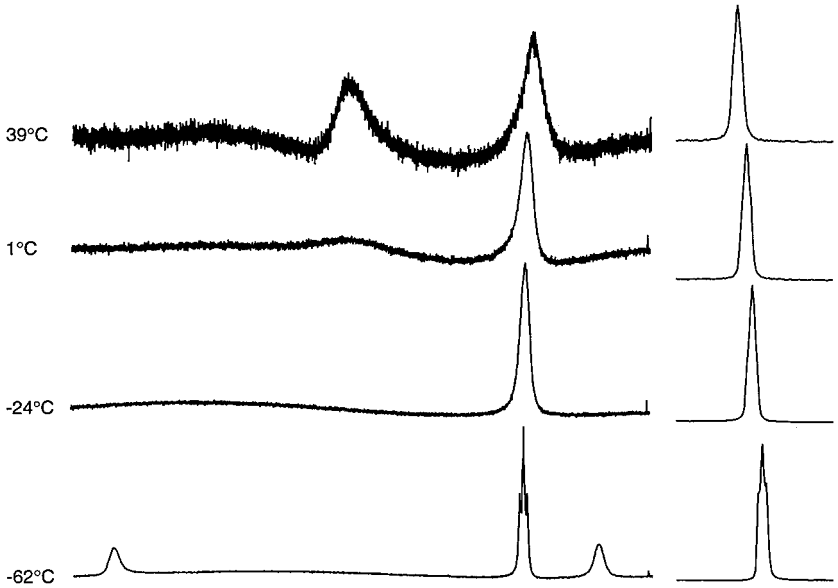
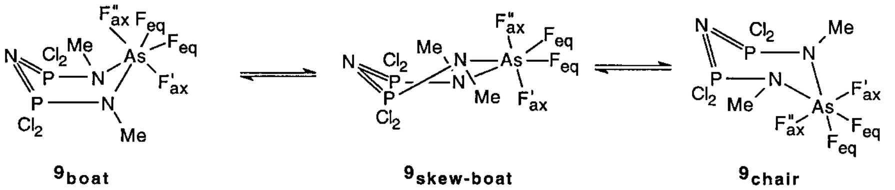


Figure 8. Variable-temperature ^{19}F (left) and ^{31}P (right) spectra of **9** in CD_2Cl_2.

exhibit fluxional behavior in solution.[35] Consideration of the boat structure ($\mathbf{9}_{boat}$) determined by X-ray crystallography suggests that three types of chemically different fluorine environments should be observed (two types of F_{ax} (F'_{ax} and F''_{ax}) and one type of F_{eq}). If the axial environments were exchanging rapidly in a boat/chair equilibrium, a single environment would be expected in the fast exchange region and two axial environments at low temperature. In addition, at least three plausible structures can be envisaged in solution (Scheme 3): the boat structure ($\mathbf{9}_{boat}$), a chair structure ($\mathbf{9}_{chair}$), and a skew-boat structure ($\mathbf{9}_{skew\text{-}boat}$), which may be considered as an intermediate between the $\mathbf{9}_{boat}$ and $\mathbf{9}_{chair}$. Thus, a variable-temperature (VT) NMR spectroscopic study of **9** was undertaken with the intention of resolving the ^{19}F NMR resonances of the fluorine atoms that are axial and equatorial to the AsN_2 moiety in compound **9** and to provide insight into the possible conformation(s) of **9** in solution.



Scheme 3. Equilibrium between the different possible conformations of **9**.

The results of these experiments are shown in Figure 8, and both the ^{31}P and ^{19}F NMR spectra (in CD_2Cl_2) are shown at each temperature. At +39 °C, a broad singlet resonance is observed in the ^{31}P NMR spectrum at $\delta = 30.6$, and two broad resonances are observed by ^{19}F NMR at approximately $\delta = -40$ and -55.[36] Upon cooling to 1 °C, the ^{31}P NMR spectrum is unchanged; however, the ^{19}F NMR spectrum shows a sharpening of the resonance at $\delta = -55$, and the broad resonance at $\delta = -40$ is much less intense. The peak in the ^{19}F NMR spectrum at $\delta = -40$ is not seen at around -5 °C and reappears as two broad resonances at about -40 °C ($\delta =$ ca. -14 and ca. -64), which is consistent with the coalescence of the two axial fluorine environments. The ^{19}F NMR signals sharpen dramatically on further cooling until the expected three sets of triplets for coupling between the F_{ax} and F_{eq} are observed in a 1:2:1 ratio at -99 °C. The equatorial fluorine atoms (F_{eq}) were observed at $\delta = -55.9$ ($^2J_{FF} = 110$ Hz) and the axial fluorine atoms F'_{ax}, which are external to the ring and in a similar chemical environment to F_{eq}, are observed at $\delta = -65.5$ ($^2J_{FF} = 105$ Hz). The axial fluorine atoms F''_{ax}, which are internal to the ring and in a dramatically different chemical environment to F_{eq} and F''_{ax}, are shifted to $\delta = -14.6$ ($^2J_{FF} = 114$ Hz). An activation energy ($\Delta G^{\neq}_{c}$) for this process of 41 ± 2 kJ mol^{-1} was estimated from the T_c (251 ± 10 K) and $\Delta\tilde{\nu}$ (14350 Hz). At -99 °C, each of the triplets for the axial fluorine atoms are split by approximately 15.5 Hz (see expansion of F''_{ax} Figure 8). This could be due to the *trans* coupling between the two nonequivalent axial fluorine atoms; however, this is typically near-zero and is not observed in species such as the $[As_2F_{11}]^-$ anion.[37] To confirm this a ^{19}F–^{19}F COSY NMR at -90 °C was undertaken to determine whether the $F_{ax}-F_{ax}$ coupling could be detected. The spectrum (Figure 9) showed the expected coupling between the peaks assigned to the axial fluorine atoms (F'_{ax} and F''_{ax}) with the two equivalent equatorial fluorine atoms (F_{eq}); however, no coupling between the axial fluorine atoms was detected. We therefore postulate that the two sets of triplets observed for the axial fluorines are from different conformational isomers.

Whereas the ^{19}F NMR signals coalesce between -5 and -40 °C, the ^{31}P NMR spectrum remains unchanged until -62 °C at which point two shoulders are observed on either side of the peak at $\delta = 30.2$. At -74 °C three distinct phosphorus environments are observed, suggesting three different compounds are present in solution at that temperature in approximately equal amounts. A possible explanation for this is that the three conformers $\mathbf{9}_{boat}$, $\mathbf{9}_{skew\text{-}boat}$, and $\mathbf{9}_{chair}$ are observed. At -99 °C the central peak is not observed, which suggests that two of these conformers freeze out at this temperature. This is also observed with the small splitting of the axial signals [F'_{ax} and F''_{ax}] in the ^{19}F NMR spectrum at -99 °C (see expansion in Figure 8). At 39 °C the central resonance is dominant, indicating that one conformer is dominant; however, close examination reveals that this resonance is slightly broad. It is beyond the scope of this study to determine which conformers are present at each temperature; however, it seems likely that $\mathbf{9}_{boat}$ is present at low temperature, since this is the conformer observed in the crystal structure. As chair isomers are generally more stable than their boat counterparts, $\mathbf{9}_{chair}$ would be expected to be stable at low temperature. We tentatively postulate that $\mathbf{9}_{skew\text{-}boat}$ may therefore only be present at elevated temperatures as an intermediate for the interconversion of $\mathbf{9}_{boat}$ and $\mathbf{9}_{chair}$.

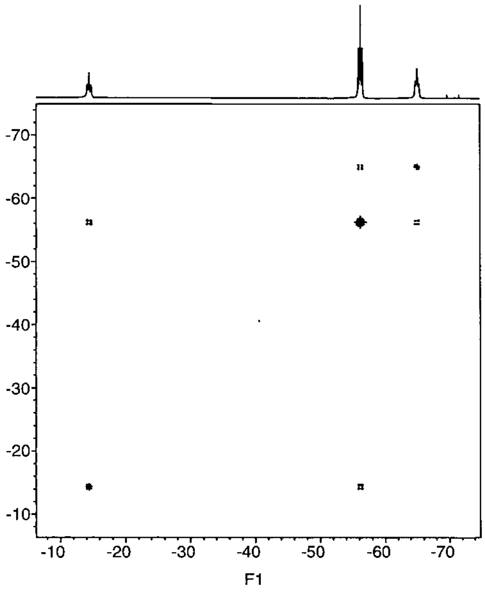
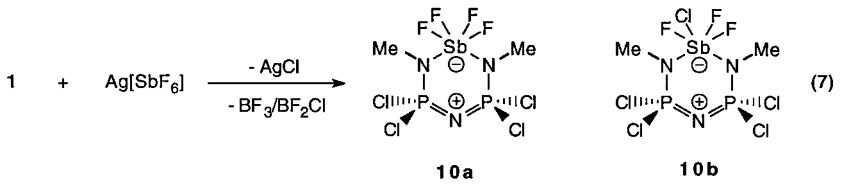


Figure 9. ^{19}F–^{19}F COSY NMR spectrum of **9** in CD_2Cl_2 at -90 °C.

*2) Skeletal substitution reaction of **1** with Ag[SbF$_6$]*: Skeletal substitution reactions of an atom in an inorganic ring are rare and, to the best of our knowledge, are unprecedented for boron-containing rings. The reactions of titanocene chalcogenide heterocycles with Group 16 dihalides to form rings in which titanium has been replaced by a chalcogen atom have been explored extensively.[38] Zirconium metallacycles have been used to prepare various main group heterocycles containing P, As, Ge, S, Ga, and so forth.[39–41] In addition, *trans*-metallation reactions of SnS_2N_2 rings with Pt complexes to yield PtS_2N_2 rings have also been observed.[42] Moreover, we assume that the cation [**2**]$^+$ is formed initially in the reaction mixture containing **1** and Ag[AsF$_6$], and the subsequent skeletal replacement of boron in a borazine-like environment would be highly unexpected. It is also noteworthy that [AsF$_6$]$^-$ is often used as a noncoordinating anion to isolate reactive cations. Remarkably, this anion appears to react readily with the borazine–phosphazene cation. We believe that the thermodynamic driving force for the observed reaction is the formation of B–F bonds from As–F bonds (B–F, 613 ± 53 kJ mol^{-1}, As–F, ca. 406 kJ mol^{-1})[43] and the subsequent elimination of volatile BF_xCl_{3-x}.

In order to explore the generality of this new synthetic procedure, we also studied the reaction of **1** with Ag[SbF$_6$] [Equation (7)]. Again, an immediate white precipitate of AgCl formed and a pressure buildup was detected. After workup, a crystalline solid (**10**) was obtained and analysis by ^{31}P NMR in $CDCl_3$ revealed two dominant resonances at δ = 28.9 and 27.5. This is consistent with skeletal replacement of boron, but suggests that more than one product is obtained from this reaction. Mass-spectral analysis indicated that both **10a** and **10b** were formed, which was confirmed by X-ray crystallographic analysis.



The molecular structure of **10a** and **10b** is shown in Figure 10, and confirms the replacement of the skeletal boron atom by antimony(v). Both compounds co-crystallize and there is occupational disorder of one atom (labeled ClF) in which Cl occupies the site 85 % of the time and F occupies it 15 % of the time. This structure is similar to that of **9** in which the ring also adopts a boat conformation. The structure of the phosphazene end of the molecule is similar to that of **1** and **9**, with the P-N-P bonds [P(1)–N(1) and P(2)–N(2)] averaging 1.560(8) Å and the P–N(Me) bonds [P(1)–N(2) and P(2)–N(3)] averaging 1.584(8) Å. The Sb(v)–N distances (av 2.072(8) Å) are similar to the average Sb(III)–N bond length (2.03 Å) in the antimony(III)cyclophosphazene, [N{P(NMe$_2$)$_2$NH}$_2$Sb(OOCMe)$_2$].[44] Few examples of Sb(v)–N-containing heterocycles have been crystallographically characterized. The Sb–N bond length in [Cl$_4$SbN(Me)C(O)C(NHMe)O] is 2.04 Å,[45] and, in a more recent example, {[Cl$_4$SbN(PMe$_3$)Sb(Cl)N(PMe$_3$)]CH$_3$CN}$^+$ the Sb(v)–N bond lengths average 2.06 Å.[46]

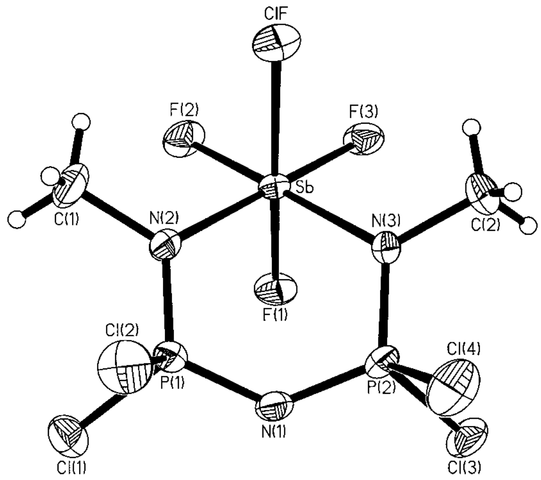


Figure 10. Molecular structure of **10** with thermal ellipsoids at the 30 % probability level. Selected bond lengths [Å] and angles [°]: Sb–N(2) 2.064(6), N(2)–P(1) 1.581(6), P(1)–N(1) 1.562(6), N(1)–P(2) 1.557(6), P(2)–N(3) 1.588(6), N(3)–Sb 2.081(5), Sb–F(1) 1.891(4), Sb–F(2) 1.906(4), Sb–F(3) 1.892(4), Sb–ClF 2.275(2); P(1)-N(1)-P(2) 128.1(4), N(1)-P(1)-N(2) 113.8(2), N(1)-P(2)-N(3) 114.0(3), P(1)-N(2)-Sb 120.4(3) N(2)-Sb-N(3) 92.2(2).

It is noteworthy that both **9** and **10** represent rare examples of heterophosphazenes containing heavier Group 15 elements in a high oxidation state. The arsazene (NAsPh$_2$)$_3$ and the arsaphosphazene hybrid (NAsPh$_2$)(NPPh$_2$)$_2$ have been synthesized and crystallographically characterized.[34, 47] To our knowledge there are no crystallographically characterized examples of antimony(v) heterophosphazene rings.[48] In this case the more electron-withdrawing fluorine atoms may provide a stabilizing effect for the high oxidation states present for the skeletal As and Sb centers.

Is there skeletal replacement in the reaction of 1 and Ag[BF$_4$] to form 8?

A ^{10}B labeling study: In order to determine whether a similar skeletal substitution reaction was occurring when Ag[BF$_4$] was treated with the boratophosphazene, a ^{10}B labeling study was undertaken. The boratophosphazene **1** was prepared from 99 % ^{10}B enriched $BF_3 \cdot OEt_2$. ^{10}B and ^{31}P NMR analysis of **1** (99 % ^{10}B) was consistent with the natural-abundance spectrum, however the ^{31}P NMR was slightly broader and no coupling was observed. In addition, the ^{11}B NMR spectrum was quite weak, indicating a very small amount of ^{11}B compound was present. When the product of the reaction of boratophosphazene **1** with Ag[BF$_4$] in CD_2Cl_2 was analyzed by ^{31}P NMR, the fluorinated boratophosphazene **8** was observed as a pseudoquartet resonance (δ = 29.0), which suggested that ^{10}B had been replaced as coupling to ^{11}B was observed. Further evidence of this was provided by examination of the ^{10}B and ^{11}B NMR spectra of the reaction mixture

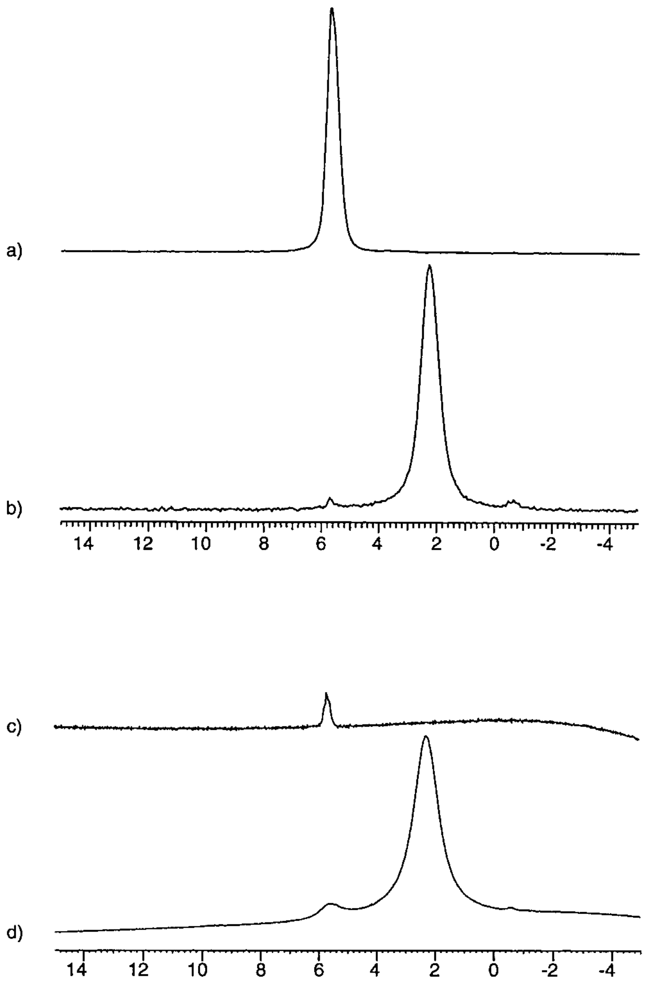


Figure 11. ^{10}B labeling study of the replacement reaction between **1** (99% ^{10}B) and $AgBF_4$ in CD_2Cl_2. a) ^{10}B NMR spectrum of **1** (99% ^{10}B); b) ^{10}B NMR spectrum after the reaction with $AgBF_4$; c) ^{11}B NMR spectrum of **1** (99% ^{10}B); d) ^{11}B NMR spectrum after the reaction with $AgBF_4$.

(Figure 11). In the ^{10}B NMR spectrum the signal for **1** had been consumed and a new resonance was formed at $\delta = 2.3$. In addition, ^{11}B NMR analysis of the reaction mixture showed that the weak ^{11}B signal for **1** (99% ^{10}B; $\delta = 5.7$) had been consumed and a strong signal had formed at $\delta = 2.3$. The ^{10}B and ^{11}B NMR spectra were consistent with the formation of **8** (δ ^{11}B (CD_2Cl_2) = 2.3). The improvement in the signal-to-noise ratio for the ^{11}B NMR spectrum of the product when compared with that for the starting material (which had ca. 1% ^{11}B) suggested that the product contained ^{11}B at or near natural abundance.[49] Furthermore, mass spectral analysis of the product showed a molecular ion ($[M^+] = 323$, 325, 327, 329) that was assigned to **8** containing ^{11}B, and the spectrum also exhibited peaks at 322, 324, 326, 328 that were assigned to either $[M^+ - H]$ (for **8** containing ^{11}B) or $[M^+]$ (for **8** containing ^{10}B). From these results it is clear that substantial skeletal replacement of the ^{10}B atom in **1** by the $[BF_4]^-$ anion (natural abundance: 80% ^{11}B, 20% ^{10}B) must have taken place in the reaction. However, it is difficult to quantify the degree of exchange between ^{10}B in **1** and $^{11}B/^{10}B$ in $[BF_4]^-$ by mass spectrometry as the $[M^+ - H]$ ion (for **8** containing ^{11}B) overlaps with $[M^+]$ (for **8** containing ^{10}B) and, furthermore, $[M^+ - H]$ is predominant in the mass spectrum of **8** formed from **1** with natural-abundance boron.

In order to investigate the necessary formation of volatile boranes ($^{10}BF_xCl_{3-x}$) the reaction was attempted in a sealed NMR tube. The two solids were mixed in an NMR tube, degassed solvent (CD_2Cl_2) was condensed into the tube, and the tube was flame-sealed. Remarkably, upon warming to room temperature no reaction was detected by ^{31}P, ^{11}B, or ^{10}B NMR spectroscopy, even after prolonged periods (weeks), and only resonances assignable to starting material were observed. When the tube was broken inside the glovebox, immediate bubbling occurred and a rapid reaction was observed forming a white precipitate (AgCl). The results of the analysis of the reaction mixture by ^{31}P, ^{10}B, and ^{11}B NMR spectroscopy were consistent with the formation of **8**. These results surprisingly indicate that the whole reaction (not just subsequent steps) is driven by the elimination of the borane.

Summary

The reactivity of the boratophosphazene **1** with halide acceptors has been studied in detail. Reaction with $AlCl_3$, $GaCl_3$, and BCl_3 gave the first well-characterized examples of borazine–phosphazene hybrids [**2**][$AlCl_4$], [**2**][$GaCl_4$], and [**2**][BCl_4], respectively, which were characterized crystallographically and spectroscopically. The structures show planar rings with bond lengths typical for borazines and phosphazenes; however for [**2**][BCl_4] evidence for coordination between the anion and the cation was observed in solution. Amines were found to react in a nucleophilic substitution reaction with the tetrachlorogallate anion of [**2**][$GaCl_4$], which was accompanied by back-coordination of chloride to $[\mathbf{2}]^+$ and reformation of **1**. Two other examples of boratophosphazenes, **7** and **8**, were synthesized by the reaction of **1** with $Ag[OSO_2CF_3]$ and $Ag[BF_4]$, respectively. Novel examples of skeletal substitution reactions were discovered by treatment of **1** with $Ag[AsF_6]$ and $Ag[SbF_6]$ resulting in the replacement of boron in a borazine-like environment by arsenic(v) or antimony(v) generating the heterophosphazenes **9**, and **10a** and **10b**. Although the compounds crystallized in the boat conformation, variable-temperature NMR analysis of **9** suggested an interconversion between the boat and chair conformations in solution. A ^{10}B labeling study of the reaction of **1** with $Ag[BF_4]$ showed that this reaction, remarkably, also involves appreciable skeletal replacement of the boron atom in **1** by the boron atom in the tetrafluoroborate anion. Detailed studies of the intriguing mechanism(s) of the skeletal substitution reactions are underway and work on the ROP behavior of **1** and related species is ongoing.

Experimental Section

General procedures: Reagents: $BF_3 \cdot OEt_2$ (Aldrich), NH_3 (Liquid Carbonic), $^{10}BF_3 \cdot OEt_2$ (Aldrich), PCl_5 (Aldrich), BCl_3 (1M in CH_2Cl_2) (Aldrich), and quinuclidine (Aldrich) were used as received; $MeNH_3Cl$ (Aldrich) was dried in vacuo (100 °C, $1x10^{-3}$ mmHg); $GaCl_3$ (Aldrich) and

$AlCl_3$ (Aldrich) were sublimed before use; NEt_3 (Aldrich) was dried over Na and distilled before use. Silver(I) salts: $Ag[OSO_2CF_3]$ (Aldrich), $Ag[BF_4]$ (Aldrich), $Ag[AsF_6]$ (Strem or Aldrich), and $Ag[SbF_6]$ (Strem or Aldrich) were dried in vacuo (ca. 120 °C, 1×10^{-3} mmHg) for about 24 h before use.[50] The salt $[Cl_3P{=}N{=}PCl_3]BCl_4$ was prepared by a literature procedure.[51] Glass wool was treated with Me_3SiCl, washed with hexanes, and dried before use. ^{31}P NMR spectra (121.4 MHz) were referenced externally to 85 % H_3PO_4; ^{13}C NMR spectra (75.4 MHz) were referenced to deuterated solvent; ^{1}H NMR spectra (300.0 MHz) were referenced to residual protonated solvent; ^{19}F NMR spectra (282.3 MHz) were referenced externally to $CFCl_3/CDCl_3$, and all were recorded on a Varian Gemini 300 spectrometer. Variable-temperature NMR spectroscopic studies were done on a Varian Gemini 300, and were referenced externally to $CFCl_3/CDCl_3$ (^{19}F) or 85 % H_3PO_4 (^{31}P) at room temperature, and the temperatures were calibrated with CH_3OH. The $^{19}F-^{19}F$ COSY NMR spectrum was recorded on a Varian XL-400 NMR spectrometer. ^{11}B NMR spectra were referenced to $BF_3 \cdot OEt_2$ and recorded on either a Gemini 300 at 96.2 MHz or a Varian 500 at 160.4 MHz. ^{10}B NMR were referenced to $BF_3 \cdot OEt_2$ and recorded on a Gemini 300 instrument. Mass spectra were obtained with a VG 70-250S mass spectrometer operating in electron impact (EI) mode. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ. All manipulations were performed in an Innovative Technology glove box or with standard Schlenck techniques, and some reactions were carried out in an evacuated chamber.[52]

Crystallographic structural determination: Crystal, data collection, and refinement parameters are given in Tables 2–4. In all cases, a suitable crystal for single-crystal X-ray diffraction was selected and mounted in a nitrogen-flushed, thin-walled glass capillary and flame sealed. All crystallographic data were collected on a Siemens P4 diffractometer with graphite monochromator, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å); for **[2]**$[AlCl_4]$ and **[2]**$[BCl_4]$ the diffractometer was equipped with a SMART CCD detector. No symmetry higher than triclinic was observed in either the photographic or diffraction data for **[2]**$[AlCl_4]$, **[2]**$[GaCl_4]$, or **7**, and the systematic absences in the diffraction data were consistent with a monoclinic crystal system, C-centered lattice for **[2]**$[BCl_4]$, and the reported space groups for **1**, **8**, **9**, and **10**. E statistics suggested the centrosymmetric space group option for **[2]**$[AlCl_4]$, **[2]**$[GaCl_4]$, and **7**. The absence of a molecular mirror plane or a two-fold axis in **[2]**$[BCl_4]$, the multiplicity, and the *E* statistics suggested the noncentrosymmetric space group *Cc* for **[2]**$[BCl_4]$. Solution in the respective space groups yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures. Semiempirical absorption corrections were applied for **9** and **10**, and no absorption corrections were required for the others, because there was less than 10 % variation in the integrated-scan intensity data. There are two independent, but chemically equivalent molecules in the asymmetric unit of **7**. The chlorine on antimony in **10** is occupationally disordered as chlorine/fluorine (85:15), modeled as an undersized chlorine atom, and labeled ClF. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI). Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 ; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-58352 (**1**), -408852 (**[2]**$[AlCl_4]$), -58352 (**[2]**$[GaCl_4]$), -408851 (**[2]**$[BCl_4]$), -408847 (**7**), -408849 (**8**), -408850 (**9**), and -408848 (**10**).

Table 2. Structural parameters for **1**, **[2]**$[AlCl_4]$, **[2]**$[GaCl_4]$ and **[2]**$[BCl_4]$

	1	**[2]**$[AlCl_4]$	**[2]**$[GaCl_4]$	**[2]**$[BCl_4]$
formula	$C_2H_6BCl_6N_3P_2$	$C_2H_6AlBCl_9N_3P_2$	$C_2H_6BCl_9GaN_3P_2$	$C_2H_6B_2Cl_9N_3P_2$
M_r	357.6	490.88	533.6	474.71
crystal class	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	Cc
color	colorless	colorless	colorless	colorless
a [Å]	9.119(2)	8.55260(10)	8.613(2)	10.6433(8)
b [Å]	7.765(2)	9.2472(2)	9.259(3)	13.2638(10)
c [Å]	18.862(4)	12.7157(2)	12.712(3)	12.2964(10)
α [°]	90	93.3693(3)	93.34	90
β [°]	103.50(3)	101.3650(10)	100.96(2)	95.6500(10)
γ [°]	90	112.7991(2)	112.71(2)	90
Z	4	2	2	4
T [K]	298	223(2)	297	223(2)
R_1 [$I > 2\sigma(I)$]	4.82	4.08	4.79	3.55
wR_2 (all data)	7.06	13.44	5.97	12.76
GOF	1.50	1.010	1.23	1.135

Table 3. Structural parameters for **7** and **8**.

	7	**8**
formula	$C_4H_6BCl_4F_6N_3O_6P_2S_2$	$C_2H_6BCl_4F_2N_3P_2$
M_r	584.79	324.65
crystal class	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
color	colorless	colorless
a [Å]	12.9815(12)	8.679(1)
b [Å]	13.6426(12)	10.583(1)
c [Å]	14.141(2)	13.161(2)
α [°]	71.576(10)	90
β [°]	62.702(5)	100.18(1)
γ [°]	77.082(8)	90
Z	4	4
T [K]	298(2)	233(2)
R_1 [$I > 2\sigma(I)$]	5.21	3.99
wR_2 (all data)	17.86	10.28
GOF	0.977	1.440

Table 4. Structural parameters for **9** and **10**.

	9	**10**
formula	$C_2H_6AsCl_4F_4N_3P_2$	$C_2H_6Cl_5F_3N_3P_2Sb$
M_r	426.76	490.04
crystal class	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
color	colorless	colorless
a [Å]	6.424(5)	6.447(2)
b [Å]	12.531(8)	17.517(5)
c [Å]	16.129(3)	12.535(3)
α [°]	90	90
β [°]	95.90(3)	97.09(4)
γ [°]	90	90
Z	4	4
T [K]	298(2)	233(2)
R_1 [$I > 2\sigma(I)$]	3.35	3.40
wR_2 (all data)	8.25	9.13
GOF	1.117	1.007

Preparation of boratophosphazene 1: This compound was prepared by a modification of the previously reported method.[16] The salts $[Cl_3P{=}N{=}PCl_3][BCl_4]$ (121.2 g, 0.275 mol) and $(MeNH_3)Cl$ (63.7 g, 0.943 mol) were slurried in 1,2-dichloroethane (ca. 300 mL) and the mixture was refluxed for 24 h. The remaining $(MeNH_3)Cl$ was removed by filtration and the solvent was removed in vacuo yielding a white solid. The crude product was recrystallized by cooling (−30 °C) the solution of **1** in hexanes/CH_2Cl_2 (1:1). Yield = 70.1 g (71 %). The ^{31}P NMR and ^{11}B NMR spectra of this compound were as previously reported in 1,2-dichloroethane.[28] ^{31}P NMR ($CDCl_3$): $\delta = 28.2$ (q, $^2J_{BP} = 15$ Hz); ^{11}B NMR ($CDCl_3$): $\delta = 5.4$ (t, $^2J_{BP} = 15$ Hz); ^{1}H NMR ($CDCl_3$): $\delta = 3.23$ (m); ^{13}C NMR ($CDCl_3$): $\delta = 33.3$; MS (EI, 70 eV): *m/z* (%): 695 (0.5) $[N_6P_6Cl_{12}^+]$, 659 (1) $[N_6P_6Cl_{11}^+]$, 544 (1.4) $[N_5P_5Cl_9^+]$, 464 (1.4) $[N_4P_4Cl_8^+]$, 427 (4.5) $[N_4P_4Cl_7^+]$, 312 (11) $[N_3P_3Cl_5^+]$, 257 (17) $[M^+ - 2\,MeCl]$, 228 (100) $[Cl_3P{=}NMe{-}BCl{=}NH^+]$, 225 (63) $[(MeNBCl)_3^+ - H]$, 193 (70) $[Cl_2P{=}NMe\text{-}BCl{=}NH^+]$.

Preparation of 1 (99 % ^{10}B): ^{10}B-enriched **1** was prepared from $^{10}BF_3 \cdot OEt_2$ (99 % ^{10}B), following the same procedure as for the unlabeled compound **1**. ^{31}P NMR (CD_2Cl_2): $\delta = 27.9$; ^{10}B NMR (CD_2Cl_2): 5.7; ^{11}B NMR (CD_2Cl_2): $\delta = 5.7$ (weak); ^{1}H NMR(CD_2Cl_2): $\delta = 3.05$ (m).

Syntheses of borazine – phosphazene hybrid cations.

*Preparation of [**2**][AlCl$_4$]*: A suspension of $AlCl_3$ (1.37 g, 10.3 mmol) in CH_2Cl_2 (30 mL) was added to a colorless solution of **1** (3.65 g, 10.2 mmol) in CH_2Cl_2 (30 mL) at room temperature. After stirring for about 1 h the solution was clear and colorless and the solvent was removed in vacuo yielding a colorless crystalline solid. The product was recrystallized by cooling (–30 °C) a CH_2Cl_2/hexanes (1:1) solution, which gave colorless crystals suitable for X-ray analysis. Yield: 4.53 g (90 %); ^{31}P NMR ($CDCl_3$): $\delta = 34.8$; ^{11}B NMR ($CDCl_3$): $\delta = 29.6$; ^{1}H NMR ($CDCl_3$): $\delta = 3.32$ (m); ^{13}C NMR ($CDCl_3$): $\delta = 35.5$.

*Preparation of [**2**][GaCl$_4$]*: A solution of $GaCl_3$ (0.26 g, 1.5 mmol) in CH_2Cl_2 (30 mL) was added to a solution of **1** (0.52 g, 1.4 mmol) in CH_2Cl_2 (30 mL). A slight yellowing of the solution was observed after stirring, and reaction was quantitative by ^{31}P NMR. The solvent was removed in vacuo yielding a beige solid. The obtained solid was dissolved in CH_2Cl_2 (2 mL) and cooled to –30 °C, and hexanes (2 mL) were layered over the top. Upon mixing at –30 °C colorless crystals formed. Yield: 0.63 g (81 %); ^{31}P NMR ($CDCl_3$): $\delta = 35.0$; ^{11}B NMR ($CDCl_3$): $\delta = 30.2$; ^{1}H NMR ($CDCl_3$): $\delta = 3.36$ (m); ^{13}C NMR ($CDCl_3$): $\delta = 35.7$; $C_2H_6BCl_9GaN_3P_2$: calcd C 4.50, H 1.13, N 7.87; found C 4.50, H 1.12, N 7.72.

*Preparation of [**2**][BCl$_4$]*: A solution of BCl_3 (1M, 1.5 mL, 1.5 mmol) in CH_2Cl_2 was added slowly to a colorless solution of **1** (0.51 g, 1.4 mmol) in CH_2Cl_2 (40 mL) by syringe at room temperature. The reaction mixture was stirred for 4 h and the solvent was removed in vacuo leaving a colorless solid. The solid was recrystallized by cooling a CH_2Cl_2/hexanes (2:1) solution to –30 °C, which yielded colorless crystals. Yield: 0.59 g (87 %); ^{31}P NMR ($CDCl_3$): $\delta = 28.4$; ^{11}B NMR ($CDCl_3$): $\delta = 6.5, 40.2$; ^{1}H NMR ($CDCl_3$): $\delta = 3.09$ (m); ^{13}C NMR ($CDCl_3$): $\delta = 33.5$.

Reaction of 1 and excess of BCl$_3$ (20 %): A solution of BCl_3 (1M, 0.35 mL, 0.35 mmol) was added to a stirred solution of **1** (0.10 g, 0.28 mmol) in CD_2Cl_2 (ca. 1.5 mL) and after about 30 min, the colorless solution was transferred to an NMR tube for analysis. ^{31}P NMR (CD_2Cl_2): $\delta = 30.0, 34.7$; ^{11}B NMR (CD_2Cl_2): $\delta = 12.3, 29.9$.

Reaction of 1 (99 % ^{10}B) with 1 equiv BCl$_3$: A solution of BCl_3 (1M, 0.20 mL, 0.20 mmol) was added to a stirred solution of **1** (99 % ^{10}B, 70 mg, 0.20 mmol) in CD_2Cl_2 (ca. 1.5 mL) and after about 30 min, the colorless solution was transferred to an NMR tube for analysis. No changes were observed in the NMR spectra after about 2 h. ^{31}P NMR (CD_2Cl_2):$\delta = 32.9$; ^{10}B NMR (CD_2Cl_2): $\delta = 10.6, 24.6$; ^{11}B NMR (CD_2Cl_2):$\delta = 10.4$.

Reactivity of borazine – phosphazene hybrid cations.

*Reaction of [**2**][GaCl$_4$] with NEt$_3$*: A solution of NEt_3 in CH_2Cl_2 (0.071M, 18.5 mL, 1.3 mmol) was added to a solution of [**2**][$GaCl_4$] (0.68 g, 1.3 mmol) in CH_2Cl_2 (ca. 30 mL). No color change was observed after stirring for 12 h, and the solvent was removed in vacuo, yielding a yellow oily material. This was then dissolved in a minimum of CH_2Cl_2 (ca. 5 mL), and was recrystallized at –30 °C. Two types of crystals were obtained, and were characterised by X-ray analysis as $Cl_3Ga \cdot NEt_3$ and boratophosphazene **1**.[27] ^{31}P and ^{11}B NMR spectroscopy were consistent with **1**.

*Reaction of [**2**][GaCl$_4$] with quinuclidine*: A solution of [**2**][$GaCl_4$] was prepared in situ from the addition of $GaCl_3$ (49 mg, 0.28 mmol) in $CDCl_3$ (0.5 mL) to **1** (100 mg, 0.28 mmol) in $CDCl_3$ (0.5 mL). ^{31}P and ^{11}B NMR confirmed the quantitative formation of [**2**][$GaCl_4$]. Quinuclidine (31 mg, 0.28 mmol) was added to this solution. ^{31}P NMR analysis of the solution revealed two quartet resonances at $\delta = 36.2$ (ca. 70 %) and $\delta = 28.0$ (ca. 30 %). ^{11}B NMR analysis revealed two overlapping resonances at $\delta = 6.5$ and 5.9. The reaction was repeated several times on a large scale in CH_2Cl_2 with similar ^{31}P and ^{11}B NMR spectra; however, fractional recrystallization (CH_2Cl_2/hexanes) was not able to completely separate the two products.

Reactions of boratophosphazene 1 with silver(I) salts.

*Reaction of **1** with Ag[OSO$_2$CF$_3$]*: A colorless solution of **1** (0.52 g, 1.5 mmol) in CH_2Cl_2 (ca. 5 mL) was added to a stirred suspension of $Ag[OSO_2CF_3]$ (0.38 g, 1.5 mmol) in CH_2Cl_2 (ca. 5 mL). The reaction mixture was stirred for about 12 h and the colorless supernatant solution was decanted from a white solid, and ^{31}P and ^{11}B NMR spectra were obtained. ^{31}P NMR (CH_2Cl_2): $\delta = 28.0$ (ca. 25 %, **1**), 29.1 (ca. 50 %, **6**), 30.6 (ca. 25 %, **7**); ^{11}B NMR (CH_2Cl_2): $\delta = 1.6$ (ca. 25 %, **7**), 4.3 (ca. 50 %, **6**), 5.5 (ca. 25 %, **1**).

*Preparation of **7***: A colorless solution of **1** (0.52 g, 1.5 mmol) in CH_2Cl_2 (10 mL) was added to a stirred suspension of $Ag[OSO_2CF_3]$ (0.78 g, 3.0 mmol) in CH_2Cl_2 (40 mL) at room temperature in the absence of light. After stirring for about 12 h a fine white precipitate was observed. The colorless solution was decanted through a plug of glass wool and the solvent was removed in vacuo leaving a white powder. Crude yield = 0.62 g (73 %). The solid was dissolved in a minimum of hexanes (10 mL) and cooled to –30 °C to form white crystals of **7** suitable for X-ray crystallography. Yield = 0.45 g (53 %); ^{31}P NMR ($CDCl_3$): $\delta = 30.6$ ($^{2}J_{BP} = 20$ Hz); ^{11}B NMR ($CDCl_3$): $\delta = 1.6$; ^{19}F NMR ($CDCl_3$): $\delta = -77.4$; ^{1}H NMR ($CDCl_3$): $\delta = 2.97$ (m); ^{13}C NMR ($CDCl_3$): $\delta = 31.2$ (CH_3), 118.3 (CF_3, $^{1}J_{CF} = 317$ Hz); MS (EI, 70 eV): *m/z* (%): 585 (0.5) [M^+], 552, 550, 548 (0.3, 0.7, 0.7) [$M^+ - Cl$], 442, 440, 438, 436, 434 (0.5, 4, 17, 29, 26) [$M^+ - OSO_2CF_3$], 69 (100) [CF_3^+]; HR-MS calcd for [$M^+ - Cl$] $C_4H_6{}^{11}BCl_3F_6N_3O_6P_2S_2$ 547.8236, found 547.8214; $C_4H_6BCl_4F_6N_3O_6P_2S_2$: calcd C 8.22, H 1.03, N 7.19; found C 7.80, H 1.63, N 6.65.

*Preparation of **8***: A colorless solution of **1** (0.50 g, 1.4 mmol) in CH_2Cl_2 (10 mL) was added to a beige suspension of $Ag[BF_4]$ (0.33 g, 1.7 mmol) in CH_2Cl_2 (40 mL) at room temperature in the absence of light. The immediate evolution of a gas was observed with bubbling and a pressure buildup as well as a large amount of fine white precipitate. The reaction mixture was stirred for about 12 h, and the colorless solution decanted through a plug of glass wool. The solvent was removed in vacuo, leaving a white powder. Yield = 0.41 g (90 %). Crystals suitable for X-ray analysis were obtained from slow evaporation of a dichloromethane solution of the product. ^{31}P NMR ($CDCl_3$): $\delta = 28.3$ (q, $^{2}J_{BP} = 15$ Hz); (CD_2Cl_2): $\delta = 28.8$ (q, $^{2}J_{BP} = 15$ Hz); ^{11}B NMR ($CDCl_3$): $\delta = 2.8$; (CD_2Cl_2): $\delta = 2.3$; ^{19}F NMR ($CDCl_3$): $\delta = -147.5$; ^{1}H NMR ($CDCl_3$): $\delta = 2.80$ (m); (CD_2Cl_2): $\delta = 2.93$ (m); ^{13}C NMR ($CDCl_3$): = 29.5; MS (EI, 70 eV): *m/z* (%): 329, 327, 325, 323 (2, 10, 25, 31) [M^+], 330, 328, 326, 324, 322 (1, 10, 39, 66, 56) [$M^+ - H$], 312, 310, 308, 306, 304 (7, 20, 60, 100, 83) [$M^+ - F$], 294, 292, 290, 288 (6, 14, 39, 40) [$M^+ - Cl$], 254, 252, 250, 248, 246 (9, 17, 56, 95, 79) [$M^+ - F_2BNCH_2$]; HR-MS calcd for $C_2H_5{}^{11}BCl_4F_2N_3P_2$ 321.8774, found 321.8786.

*Preparation of **9***: A solution of the boratophosphazene **1** (1.04 g, 2.91 mmol) in CH_2Cl_2 (ca. 20 mL) was added to a slurry of $Ag[AsF_6]$ (1.05 g, 3.54 mmol) in the same solvent (ca. 75 mL); this mixture was stirred at room temperature in the absence of light. An immediate fine white precipitate was observed along with a pressure buildup. The reaction was stirred for 12 h and the colorless solution was carefully decanted through a small plug of glass wool to remove AgCl. The solvent was removed in vacuo leaving a crystalline solid and a small amount of yellow oil. Extraction of the solid into a mixture of CH_2Cl_2/hexanes (ca. 1:10; twice) and subsequent removal of solvent gave pure **9** (free from hydrolysis product).[50] Yield: 0.63 g (51 %). Large colorless crystals suitable for X-ray analysis were obtained by cooling (–30 °C) a CH_2Cl_2/hexanes (1:1) solution of the product. ^{31}P NMR ($CDCl_3$): $\delta = 30.6$; ^{1}H NMR ($CDCl_3$): $\delta = 3.16$ (m); ^{13}C NMR ($CDCl_3$): $\delta = 34.1$; MS (EI, 70 eV): *m/z* (%): 431, 429, 427, 425 (2, 6, 13, 10) [M^+], 430, 428, 426, 424 (5, 15, 29, 23) [$M^+ - H$], 412, 410, 408, 406 (2, 9, 17, 12) [$M^+ - F$], 280, 278, 276, 274 (14, 58, 100, 85) [$M^+ - AsF_4$]; HR-MS calcd for $C_2H_6AsP_2Cl_4N_3F_4$ 424.7943, found 424.7932; $C_4H_6BCl_4F_6N_3O_6P_2S_2$: calcd C 5.63, H 1.42, N 9.85, found C 5.92, H 1.28, N 9.75.

*Preparation of **10a** and **10b***: A solution of the boratophosphazene **1** (0.51 g, 1.43 mmol) in CH_2Cl_2 (ca. 15 mL) was added to a slurry of $Ag[SbF_6]$ (0.52 g, 1.51 mmol) in the same solvent (ca. 40 mL) and was stirred at room temperature in the absence of light. An immediate fine white precipitate was observed along with a pressure buildup. The reaction was stirred for 12 h and the colorless solution was carefully decanted through a small plug of glass wool to remove AgCl. The solvent was removed in vacuo leaving a brown oil. Extraction into a mixture of CH_2Cl_2/hexanes(1:10) (twice) and subsequent removal of solvent gave pure **10a** and **10b** as a colorless solid. Yield = 0.51 (ca. 75 %). Colorless crystals suitable for X-ray analysis were obtained by cooling (–30 °C) a CH_2Cl_2/hexanes (1:1) solution of the product. ^{31}P NMR ($CDCl_3$): $\delta = 28.9, 27.5$; ^{1}H NMR ($CDCl_3$): $\delta = 3.23$ (m); ^{13}C NMR ($CDCl_3$): $\delta = 33.5$; MS (EI, 70 eV): *m/z* (%): 493, 491, 489, 487 (1, 1, 2, 1) [M^+(**10b**)], 494, 492, 490, 488, 486 (2, 6, 10, 11, 5) [M^+(**10b**) – H], 478, 476, 474, 472, 470 (1, 5, 13, 21, 17) [M^+(**10a**) – H], 460, 458, 456, 454, 452 (3, 15, 39, 48, 25) [M^+(**10a**) – F] and [M^+(**10b**) – Cl)], 280, 278, 276, 274 (12, 55, 100, 91) [M^+(**10a**) – SbF_4] and [M^+(**10b**) – SbF_3Cl)].

*Reaction of **1** (99 % ^{10}B) with $Ag[BF_4]$*: A solution of **1** (99 % ^{10}B) (78 mg, 0.2 mmol) in CD_2Cl_2 (ca. 0.5 mL) was added to a slurry of $Ag[BF_4]$ (43 mg, 0.2 mmol) in CD_2Cl_2 (ca. 1.5 mL) and the supernatant solution was decanted from a white precipitate into an NMR tube. ^{31}P NMR (CD_2Cl_2): $\delta = 29.0$; ^{10}B NMR (CD_2Cl_2): $\delta = 2.3$; ^{11}B NMR (CD_2Cl_2): $\delta = 2.3$; ^{19}F NMR (CD_2Cl_2): $\delta = -146$; MS (EI, 70 eV): *m/z* (%) 329, 327, 325, 323 (2, 11, 36, 54) [$M^+(^{11}B)$], 328, 326, 324, 322 (9, 32, 57, 46); [$M^+(^{10}B)$] and [$M^+ - H(^{11}B)$], and the lower mass region of the spectrum is similar to that of **8** above. For the reaction in a sealed NMR tube, the reactants were mixed as solids and degassed CD_2Cl_2 was added by vacuum condensation at −196 °C. The tube was then flame-sealed under vacuum and warmed to room temperature. ^{31}P and ^{11}B NMR exhibited only resonances assigned to **1** even after several weeks.

Acknowledgments: This work was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC). D.G. would like to thank NSERC for a Graduate Fellowship (1993–97), A.M. also thanks NSERC for a Graduate Fellowship (1996–1998), R.Z. thanks the Deutscher Akademischer Austauschdienst (DAAD) for a Postdoctoral Fellowship and I.M. is grateful to the Alfred P. Sloan Foundation for a Research Fellowship (1994–98), NSERC for an E. W. R. Steacie Fellowship (1997–1999), and the University of Toronto for a McLean Fellowship (1997–2003). The authors would also like to thank Prof. Bill Reynolds for useful discussions regarding the VT NMR behavior of **9**.

Received: February 10, 1998 [F1000]

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