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Reversible Skeletal Transmetalations of Inorganic Rings: Isolation of Aluminatophosphazenes, a Zwitterionic Phosphazene, and a Donor-Stabilized Alumazine–Phosphazene Hybrid Cation

Eric Rivard, Paul J. Ragogna,‡ Andrew R. McWilliams,† Alan J. Lough, and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George St. Toronto, Ontario, M5S 3H6, Canada

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Synthesis of the cyclic aluminatophosphazene ring $N(PCl_2NMe)_2AlMeCl$ (**5**) has been achieved via a skeletal transmetalation reaction between $AlMe_3$ and the boratophosphazene $N(PCl_2NMe)_2BCl_2$ (**1**). Reaction of **5** with various halogenated Lewis acids such as $GaCl_3$ yielded the fully chlorinated aluminum heterocycle $N(PCl_2NMe)_2AlCl_2$ (**8**) through a methyl–halogen exchange process. In contrast, treatment of **5** with excess $AlMe_3$ resulted in complete methylation at aluminum to give $N(PCl_2NMe)_2AlMe_2$ (**6**). Compound **5** was reacted with various Ag^+ salts with weakly coordinating anions, including $Ag[OSO_2CF_3]$, which afforded the triflate-substituted heterocycle $N(PCl_2NMe)_2AlMe(OSO_2CF_3)$ (**9**). The reaction of **5** with $Ag[BF_4]$ surprisingly produced the previously known fluorinated boratophosphazene $N(PCl_2NMe)_2BF_2$ (**10**). The transformation of **1** to **5** and then to **10** represents a rare, formally reversible, skeletal transmetalation process involving boron and aluminum. Treatment of **5** with $Ag[PF_6]$ led to the insertion of phosphorus in place of aluminum to form the novel zwitterionic fluorinated phosphorus(V) heterocycle $N(PCl_2NMe)_2PF_4$ (**11**). The ethyl-substituted aluminatophosphazene $N(PCl_2NMe)_2AlMeEt$ (**14**) reacted cleanly with a 1:1 mixture of $[Ph_3C][B(C_6F_5)_4]$ and THF to give the novel donor-stabilized alumazine–phosphazene hybrid cation, $[\mathbf{7{\cdot}THF}]^+$, as the $[B(C_6F_5)_4]^-$ salt $[N(PCl_2NMe)_2AlMe{\cdot}THF][B(C_6F_5)_4]$ (**15**).

Introduction

Cyclic compounds of main group elements often exhibit interesting structural motifs, display novel chemical reactivity, and pose intriguing bonding questions as a result of the variety of stable coordination numbers and oxidation states accessible.[1] As a reflection of the renewed interest in main group heterocycles, a series of cationic aluminum-based catalysts are currently being explored as alternatives to their ubiquitous transition metal counterparts (e.g., in the Ziegler–Natta polymerization of olefins).[2,3] In addition, the ring-opening polymerization (ROP) of various perhalogenated

* To whom correspondence should be addressed. E-mail: imanners@chem.utoronto.ca.

† Current address: Department of Chemistry and Biology, Ryerson University, 350 Victoria St., Toronto, Ontario, M5B 2K3, Canada.

‡ Current address: Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7, Canada.

(1) (a) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4272. (b) Scheschkewitz, D.; Gornitzka, A. H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2002**, *295*, 1880. (c) Hardman, N. J.; Power, P. P.; Gorden, J. D.; Macdonald, C. L. B.; Cowley, A. H. *Chem. Commun.* **2001**, 1866. (d) Ni, Y.; Lough, A. J.; Rheingold, A. L.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 998. (e) Guo, C.-Y.; Kirchmeier, R. L.; Shreeve, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 9000. (f) Barclay, T. M.; Cordes, A. W.; Goddard, J. D.; Mawhinney, R. C.; Oakley, R. T.; Preuss, K. E.; Reed, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 12136. (g) Brownridge, S.; Du, H.-B.; Fairhurst, S. A.; Haddon, R. C.; Oberhammer, H.; Parsons, S.; Passmore, J.; Schriver, M. J.; Sutcliffe, L. H.; Westwood, N. P. C. *J. Chem. Soc., Dalton Trans.* **2000**, 3365. (h) Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Lumsden, M.; Macdonald, C. L. B.; Phillips, A. D.; Ragogna, P. J.; Schurko, R. W.; Walsh, D.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2002**, *124*, 14012. (i) Haiduc, I. *The Chemistry of Inorganic Ring Systems, Part I and II*; Wiley-Interscience: Toronto, 1970. (j) Roesky, H. W. *Inorg. Chem.* **2004**, *43*, 7284. (k) Martin, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G.; *Angew. Chem., Int. Ed.* **2005**, *44*, 1700.

(2) For selected examples of aluminum-based heterocyclic catalysts, see: (a) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125. (b) Ihara, E.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277. (c) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523. (d) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Bruce, M. D.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 1883. (e) Duchateau, R.; Meetsma, A.; Teuben, J. H. *Chem. Commun.* **1996**, 223. (f) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 8291. (g) Yu, R.-C.; Hung, C.-H.; Huang, J.-H.; Lee, H.-Y.; Chen, J.-T. *Inorg. Chem.* **2002**, *41*, 6450. (h) Cameron, P. A.; Gibson, V. C.; Irvine, D. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2141.

(3) For selected examples of transition metal-based heterocyclic catalysts, see: (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (c) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830. (d) Mehrkhodavandi, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2001**, *123*, 10746. (e) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 3184. (f) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958. (g) Betley, T. A.; Peters, J. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 2385. (h) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

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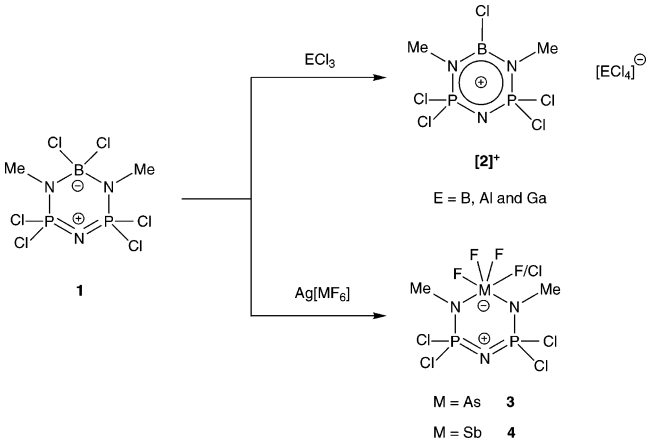
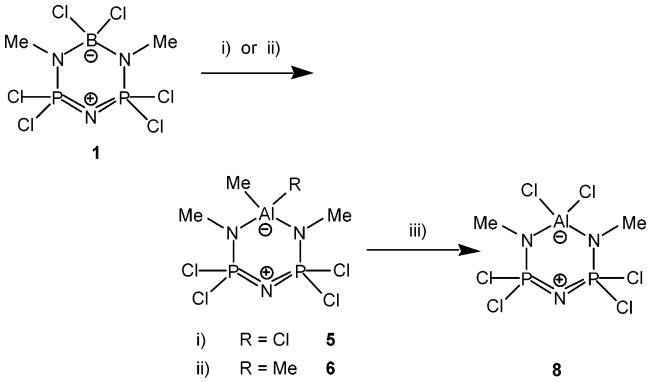
main group rings provides a number of previously unknown inorganic polymeric materials and represents one of the major avenues of research in inorganic polymer science.[4,5]

Motivated by the successful use of cyclic perhalogenated heterophosphazenes such as cyclothionylphosphazenes NS(O)X$(NPCl_2)_2$ (X = Cl and F) as polymer precursors via ROP,[6] our group has investigated the chemistry of boratophosphazenes. During the unsuccessful attempts to polymerize the cyclic boratophosphazene $N(PCl_2NMe)_2BCl_2$ (**1**), some interesting chemical reactivity was observed. Treatment of **1** with group 13 halide acceptors (ECl_3, E = B, Al, and Ga) readily afforded the planar hybrid borazine−phosphazene cations **[2]**$^+$.[7] Attempts to generate similar cations using silver(I) salts with fluorinated counteranions $[AsF_6]^-$ and $[SbF_6]^-$ remarkably led to the insertion of arsenic and antimony in place of the boron atom in **1** to give the novel group 15 heterophosphazenes **3** and **4**.[8,9] Examples of this



type of transmetalation reaction, where one atom is selectively replaced by another while retaining the original ring structure, remain rare.[10] The efficient nature of the skeletal substitution reaction coupled with the facile separation of the resulting byproducts makes this a valuable synthetic tool for the construction of new inorganic rings. This process also highlights interesting issues concerning the structure and bonding of these main group heterocycles.

Scheme 1. Synthesis of Aluminatophosphazenes **5**, **6**, and **8**[a]



[a] (i) 2 equiv of $AlMe_3$, toluene, 5 h, 20 °C. (ii) 4 equiv of $AlMe_3$, toluene, 16 h, 20 °C. (iii) 1 equiv of either ECl_3 (E = B, Al, and Ga), $TaCl_5$, or SO_2Cl_2, CH_2Cl_2, 24 H, 20 °C.

In this context, we report the successful extension of the skeletal substitution methodology, which corresponds to a formal transmetalation process. An unusual example of a zwitterionic, phosphazene six-membered ring system is reported in conjunction with the first example of an aluminatophosphazene cation, which has potential for a significant impact in the areas of catalysis and inorganic polymer science (i.e., as ROP precursors).[11]

Results and Discussion: Synthesis of Aluminatophosphazenes

To further explore the scope of the skeletal substitution chemistry of **1**, this species was reacted with a single equivalent of $AlMe_3$ in toluene. The ^{31}P NMR spectrum of the resulting solution indicated that the complete consumption of **1** (δ = 28.8 ppm) had occurred to yield two new products (ca. 1:1 ratio), as evidenced by the appearance of upfield-shifted resonances located at δ = 23.6 and 25.3 ppm.[12] Attempts to separate the products by fractional crystallization were unsuccessful. However, when 2 equiv of $AlMe_3$ were added, complete conversion of **1** to a single phosphorus-containing product with the ^{31}P NMR resonance at δ = 23.6 ppm occurred. The ^{11}B NMR spectrum of the reaction mixture identified BMe_3 as the only boron-containing product with a chemical shift of δ = 85.9 ppm[13] (^{11}B NMR shift of **1**: δ = 5.4 ppm); this observation suggested that halogen−methyl exchange between a B−Cl group in **1** and $AlMe_3$ had transpired. Removal of the volatiles followed by recrystallization from toluene afforded highly air- and moisture-sensitive colorless crystals that did not give a ^{11}B NMR signal, indicating an absence of boron in the isolated product. The ^{1}H NMR spectrum contained a sharp singlet at δ = −0.57 ppm along with a multiplet resonance at δ =

(4) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.
(5) (a) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216. (b) Allcock, H. R. J. *Inorg. Organomet. Polym.* **1992**, *2*, 197. (c) Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1989**, *111*, 5478. (d) Dodge, J. A.; Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1990**, *112*, 1268. (e) Gates, D. P.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1997**, 2525.
(6) (a) Gates, D. P.; Edwards, M.; Liable-Sands, L. M.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **1998**, *120*, 3249. (b) McWilliams, A. R.; Gates, D. P.; Edwards, M.; Liable-Sands, L. M.; Guzei, I.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 8848. (c) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044.
(7) Gates, D. P.; Ziembinski, R.; Rheingold, A. L.; Haggerty, B. S.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2277.
(8) Gates, D. P.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **1997**, *119*, 1125.
(9) Gates, D. P.; McWilliams, A. R.; Ziembinski, R.; Liable-Sands, L. M.; Guzei, I. A.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *Chem. Eur. J.* **1998**, *4*, 1489.
(10) (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Jolliffe, J. M.; Kelly, P. F.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2179. (c) Kuhn, N.; Kuhn, A.; Lewandowski, J.; Speis, M. *Chem. Ber.* **1991**, *124*, 2197. (d) Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365. (e) Ashe, A. J., III; Fang, X.; Kampf, J. F. *Organometallics* **2001**, *20*, 2109.
(11) For a brief communication on some of this work, see; (a) McWilliams, A. R.; Rivard, E.; Lough, A. J.; Manners, I. *Chem. Commun.* **2002**, 1102. For an early report on a four-membered N−P zwitterionic ring system, see: (b) Niecke, E.; Kröher, R.; Pohl, S. *Angew. Chem., Int. Ed.* **1977**, *16*, 864.
(12) The reaction of hexachlorocyclotriphosphazene $[Cl_2P{=}N]_3$ with excess $AlMe_3$ produces a complex mixture of partially methylated phosphazene rings: Harris, P. J.; Jackson, L. A. *Organometallics* **1983**, *2*, 1477.
(13) The reported ^{11}B NMR shift for BMe_3 in toluene is δ = 86.6: Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908.

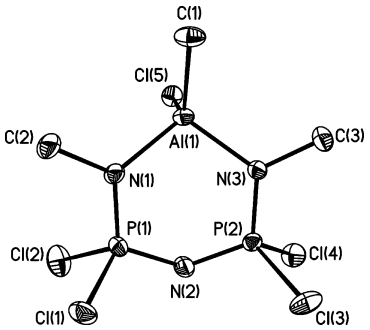
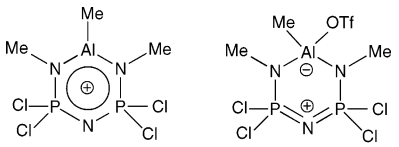


Figure 1. Molecular structure of **5** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [deg]: Al(1)−Cl(5), 2.161(1); Al(1)−N(1), 1.889(2); Al(1)−N(3), 1.889(2); P(1)−N(1), 1.575(2); P(1)−N(2), 1.563(2); P(2)−N(2), 1.562(2); P(2)−N(3), 1.574(2); N(2)−Al(1)−N(3), 103.3(1); Al(1)−N(1)−P(1), 121.1(1); N(1)−P(2)−N(2), 115.1(1); P(1)−N(2)−P(2), 130.2(2); N(2)−P(2)−N(3), 114.9(1); P(2)−N(2)−Al(1), 121.6(1); C(1)−Al(1)−Cl(5), 114.0(1).

3.23 ppm (1:2 integration ratio). On the basis of the observed integration ratio of these signals and the fact that the boratophosphazene **1** has a similar ^{1}H NMR resonance at $\delta = 3.10$ ppm (multiplet) due to the N−Me groups within the heterocycle, we assigned the product as the novel methyl-substituted aluminatophosphazene heterocycle $N(PCl_2NMe)_2AlMeCl$ (**5**) (Scheme 1). $^{13}C\{^1H\}$ NMR spectroscopy supported the formation of **5**, as the N−Me group was detected as a singlet at $\delta = 31.1$ ppm (c.f. the N−Me ^{13}C NMR resonance for **1** is at $\delta = 33.3$ ppm). However, no signal could be detected for the Al−Me moiety within **5** because of quadrupolar broadening of this resonance by the neighboring aluminum center (^{27}Al; $I = 5/2$).[14] To unequivocally identify **5** as the reaction product, we performed a single-crystal X-ray diffraction study (Figure 1) on the isolated crystalline material.[15]

In an attempt to synthesize a tetramethylated aluminatophosphazene, compound **5** was reacted with additional equivalents of $AlMe_3$ in toluene. When 1 equiv of $AlMe_3$ was added to **5**, two signals (1:1 ratio) were observed by ^{31}P NMR spectroscopy. One signal corresponded to unreacted **5** ($\delta = 23.6$ ppm), whereas a new upfield-shifted resonance was also noted at $\delta = 21.5$ ppm. Addition of excess $AlMe_3$ to the reaction mixture converted all remaining **5** to the species with the ^{31}P NMR resonance at $\delta = 21.5$ ppm. A tacky, white solid was subsequently isolated and identified as the methylated heterocycle, $N(PCl_2NMe)_2AlMe_2$ (**6**),[17] on the basis of NMR spectroscopy and mass spectrometry (Scheme 1). Analysis of **6** by ^{1}H NMR spectroscopy revealed a singlet resonance at $\delta = -0.82$ ppm which was assigned to the aluminum-bound methyl groups in addition to the expected multiplet for the N−Me group at $\delta = 2.76$ ppm. Each of these signals integrated to six protons, confirming the presence of two Al−Me groups in **6**. The $^{13}C\{^1H\}$ NMR spectrum showed the anticipated N−Me resonance ($\delta = 31.0$ ppm) along with a broad resonance due to the Al-Me groups at $\delta = -10.6$ ppm. The detection of an Al−Me $^{13}C\{^1H\}$ NMR resonance for **6** suggested that a more symmetric electronic environment was present at the aluminum center when compared to **5**, where no $^{13}C\{^1H\}$ NMR signal was observed. This is in comparison to the similar $^{13}C\{^1H\}$ NMR shift ($\delta = -10.6$ ppm) that has been reported for the Al−Me groups within the β-diketiminate complex $HC(CMeNAr)_2AlMe_2$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).[18]

Chemistry of Aluminatophosphazene 5: Discovery of Novel Skeletal Transmetalations. In previous studies, a novel class of borazine−phosphazene hybrid cations **[2]**$^+$ were synthesized from the boratophosphazene **1** using Group 13 Lewis acids (ECl_3, E = B, Al, and Ga) as halide acceptors.[7] Encouraged by these results and the presence of an apparently slightly elongated Al−Cl bond within **5** (see below), we explored the reactions of this aluminum analogue with various halide acceptors[7] with the goal of generating an alumazine−phosphazene heterocyclic cation $[N(PCl_2NMe)_2AlMe]^+$, **[7]**$^+$. When **5** was treated with 1 equiv of $GaCl_3$ in

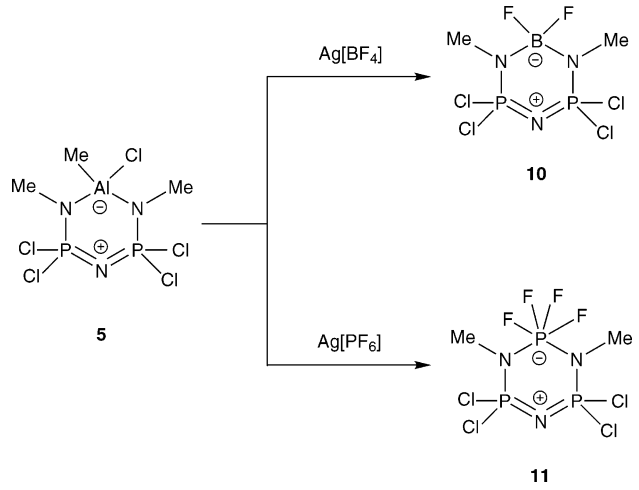


CH_2Cl_2, we observed quantitative formation of a new product after 16 h, as indicated by a new resonance at $\delta = 25.3$ ppm in the ^{31}P NMR spectrum of a sample of the reaction mixture; interestingly, a species with the same chemical shift was also observed as a component of the reaction mixture when the boratophosphazene **1** was reacted with 1 equiv of $AlMe_3$. A white solid was subsequently isolated, and large, colorless plates were then obtained from a 1:1 CH_2Cl_2/hexanes mixture at −30 °C. Single-crystal X-ray diffraction identified the product as the chlorinated heterocycle $N(PCl_2NMe)_2AlCl_2$ (**8**), unfortunately the low quality of the data ($R1 > 10\%$) precludes any detailed discussion of the bonding within this compound. ^{1}H NMR spectroscopy provided additional evidence for the formation of **8**, as a multiplet was detected at $\delta = 2.92$ ppm for the N-bonded methyl groups, while no Al−Me resonance was observed. Moreover, the molecular ion for **8** ($m/z = 373$) was detected by mass spectrometry and the product gave satisfactory elemental analyses. When **5** was reacted with the related chlorinated Lewis acids $AlCl_3$, BCl_3, $TaCl_5$, and SO_2Cl_2, similar methyl−halogen exchange reactions occurred to give **8**. It is possible that formation of the perhalogenated aluminum ring **8** proceeds via a transient aluminatophosphazene cation such as **[7]**$^+$.[19]

As the chlorination of **5** occurred in the presence of Lewis acidic chlorides, we explored the reactivity of this aluminatophosphazene toward various silver(I) salts containing

(14) Cocco, L.; Eyman, D. P. *J. Organomet. Chem.* **1979**, *179*, 1.
(15) For related Al−N−P heterocycles, see: (a) Hasselbring, R.; Roesky, H. W.; Heine, A.; Stalke, D.; Sheldrick, G. M. *Z. Naturforsch.* **1994**, *49B*, 43. (b) Burford, N.; LeBlanc, D. J. *Inorg. Chem.* **1999**, *38*, 2248. (c) Lawson, G. T.; Jacob, C.; Steiner, A. *Eur. J. Inorg. Chem.* **1999**, 1881.
(16) Burrow, R. A.; Farrar, D. H.; Honeyman, C. H. *Acta Crystallogr.* **1994**, *C50*, 681.
(17) Compound **6** can also be synthesized by the reaction of boratophosphazene **1** with excess $AlMe_3$ (4−10 equiv).
(18) Qian, B.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070.

Scheme 2. Generation of the Fluorinated Heterocycles **10** and **11** via Skeletal Substitution Chemistry



weakly coordinating anions as an alternative path to a cationic aluminatophosphazene ring. As previously noted, in the case of the boron analogue **1**, this strategy led to the discovery of a series of unusual skeletal substitution reactions.[8,9]

The reaction of **5** with a slight excess of $Ag[OSO_2CF_3]$ in dichloromethane led to the isolation of a highly moisture-sensitive, colorless oil. The ^{31}P NMR spectrum of this product in $CDCl_3$ consisted of a singlet at $\delta = 25.7$ ppm, which was shifted downfield from the ^{31}P NMR resonance of **5** ($\delta = 23.6$ ppm). A ^{19}F NMR chemical shift attributed to a triflate (OSO_2CF_3) group was observed at $\delta = -77.6$ ppm; a similar resonance was observed for triflate-substituted boratophosphazene, $N(PCl_2NMe)B(OSO_2CF_3)_2$ ($\delta = -77.4$ ppm), and this suggests that the interaction between the triflate group and the aluminum center in the product is mainly covalent in nature.[18] A quartet resonance due to the CF_3 group of the triflate was located at $\delta = 118.9$ ($^1J_{CF} = 316$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum, while the nitrogen- and aluminum-bound methyl groups appeared at $\delta = 31.1$ and -15.1 ppm, respectively (the associated ^1H NMR resonances were observed at $\delta = 2.86$ and -0.52 ppm). These data were consistent with formation of the aluminatophosphazene $N(PCl_2NMe)_2AlMe(OSO_2CF_3)$ (**9**).

When **5** was allowed to react with $Ag[BF_4]$, the quantitative formation of a new product was detected by the presence of a downfield-shifted ^{31}P NMR resonance at $\delta = 28.8$ ppm (pseudoquartet) and a singlet at $\delta = -147.5$ ppm in the ^{19}F NMR spectrum of the reaction mixture. These signals, along with the accompanying ^1H and ^{11}B NMR spectra, matched those of the previously known fluorinated boratophosphazene heterocycle, $N(PCl_2NMe)_2BF_2$, **10**.[9] This reaction represents part of a formally reversible skeletal atom substitution process involving boron and aluminum (Scheme 2). A possible mechanism of this transformation includes the initial formation of the alumazine−phosphazene cation $\mathbf{[7]}^+$ (as the BF_4^- salt) by halide abstraction followed by fluoride ion transfer from BF_4^- to $\mathbf{[7]}^+$ and the formal replacement of a MeClAl fragment by a BF_2 group. Unfortunately, no intermediates (including the $MeAlF_2$ byproduct) could be detected spectroscopically during the course of this unusual skeletal substitution reaction. The ability to exchange atoms within a cyclic heterophosphazene in a selective and reversible manner, while retaining the initial ring framework, remains a rarely investigated, yet potentially useful, reaction in inorganic chemistry.[20] As a consequence, we extended our studies of the reactivity of **5** to include other silver salts.

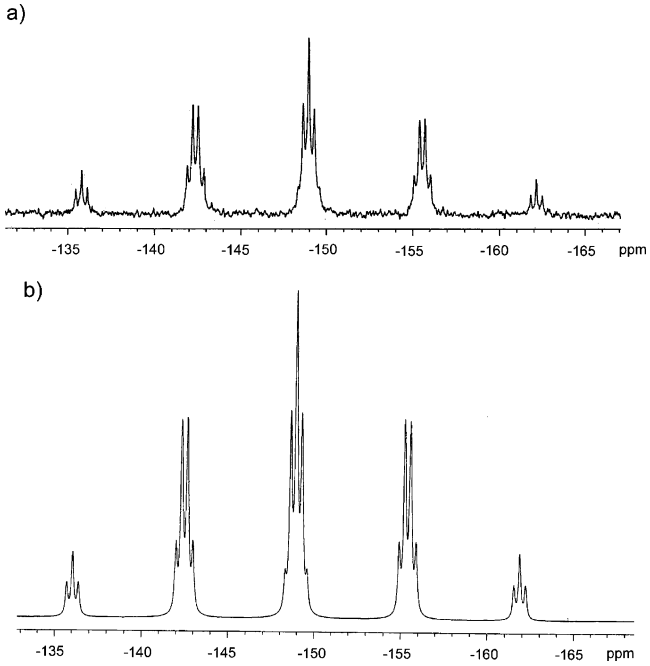


Figure 2. Experimental (a) and simulated (b) ^{31}P NMR spectra of the hexacoordinated phosphorus atom within **11** ($CDCl_3$, 121.5 MHz, 20 °C).

It is known that the hexafluorophosphate anion, $[PF_6]^-$, coordinates more weakly to cationic substrates than the tetrafluoroborate anion $[BF_4]^-$.[21] Reaction of $Ag[PF_6]$ with **5** in dichloromethane, followed by analysis of the reaction mixture by ^{31}P NMR spectroscopy indicated that the PF_6^- ion was consumed. Two new signals were detected at $\delta = 33.8$ (d, $^2J_{PP} = 40$ Hz) and -149.0 ppm (m). The latter resonance has a similar chemical shift as that in the previously reported arsenic(V) heterophosphazene ring $N(PCl_2NMe)_2AsF_4$ (**3**) ($\delta = 34.1$ ppm),[8,9] while the highly upfield-shifted multiplet is consistent with the presence of a hexacoordinate phosphorus center (c.f. free PF_6^- anion $\delta = -144.1$ ppm (heptet)).[22] A simulation of the upfield portion of the ^{31}P NMR spectra (Figure 2) revealed the presence of

(19) We also explored the reactivity of **8** towards $GaCl_3$, $AlCl_3$, and $TaCl_5$ and in all instances obtained dark red oils with downfield-shifted ^{31}P NMR resonances (26−28 ppm). All attempts to isolate pure products from these reactions have been frustrated by the extreme reactivity of the possibly cationic aluminum product.

(20) For examples of the use of skeletal substitution chemistry in organic synthesis, see: (a) Nakamoto, M.; Tilley, T. D. *Organometallics* **2001**, *20*, 5515. (b) Nitschke, J. R.; Tilley, T. D. *J. Organomet. Chem.* **2002**, *666*, 15. (c) Takahashi, T.; Ishikawa, M.; Huo, S. *J. Am. Chem. Soc.* **2002**, *124*, 388.

(21) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley-Interscience: Toronto, 1999; p 392.

(22) Cyr, P. W.; Rettig, S. J.; Patrick, B. O.; James, B. R. *Organometallics* **2002**, *21*, 4672.

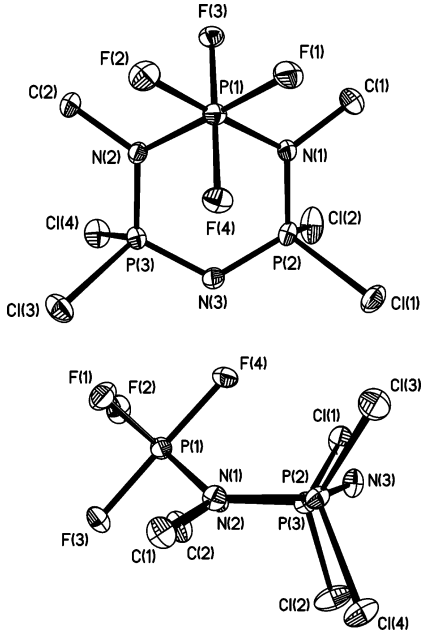


Figure 3. Molecular structure of **11** with thermal ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [deg]: F−P(1), avg 1.602(3); P(1)−N(1), 1.814(2); P(1)−N(2), 1.819(2); P(2)−N(1), 1.599(2); P(2)−N(3), 1.569(2); P(3)−N(2), 1.603(2); P(3)−N(3), 1.561(2); F(1)−P(1)−F(2), 89.4(1); F(3)−P(1)−F(4), 179.2(1); N(1)−P(1)−N(2), 92.4(1); P(1)−N(1)−P(2), 123.0(1); N(1)−P(2)−N(3), 114.7(1); P(2)−N(3)−P(3), 121.8(1); N(3)−P(3)−N(2), 114.5(1); P(3)−N(2)−P(1), 122.3(1).

an overlapping triplet of triplet of triplets [$^1J_{PF}$ = ca. 800 Hz (to equatorial F) and ca. 765 Hz (to axial F); $^2J_{PP}$ = 40 Hz],[23] and suggested that the incorporation of a phosphorus atom in place of the aluminum had occurred to give the zwitterionic cyclophosphazene, $N(PCl_2NMe)_2PF_4$ (**11**).

Confirmation of the assigned structure was obtained when a single-crystal X-ray diffraction study was performed on large, colorless, rod-shaped crystals of **11**, which were grown from toluene (−30 °C) (Figure 3). To our knowledge, compound **11** represents the only structurally characterized phosphazene heterocycle to contain both formally anionic and cationic phosphorus environments within a ring framework.[24]

Nucleophilic Substitution Chemistry of Aluminatophosphazenes. One advantage of halogenated inorganic rings stems from an increased degree of tunability due to the availability of many types of halide replacement reactions, thus providing control over the electrophilicity and subsequent reactivity of the ring. Consequently, we decided to perform further reactivity studies involving **5** and selected oxygen-, nitrogen-, and carbon-based nucleophiles.

When **5** was to reacted with Mes*OLi·OEt_2 (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) in toluene, a downfield-shifted singlet

(23) ^{31}P coupling constants were estimated by simulating the ^{31}P NMR spectra of **11** assuming an $AM_2X_2Y_2$ spin system.

(24) For related work, see: (a) Well, M.; Jones, P. G.; Schmutzler, R. *J. Fluorine Chem.* **1991**, *53*, 261. (b) Kaukorat, T.; Jones, P. G.; Schmutzler, R. *Heteratom. Chem.* **1991**, *2*, 8129. (c) Schlak, O.; Schmutzler, R.; Schiebel, H.-M.; Wazeer, M. I. M.; Harris, R. K. *J. Chem. Soc., Dalton Trans.* **1974**, 2153. (d) Hahn, H.; Toifl, E.; Meindl, W.; Utvary, K. *Monatsh. Chem.* **1984**, *115*, 881. (e) Galle, K.; Utvary, K. *Monatsh. Chem.* **1988**, *119*, 174.

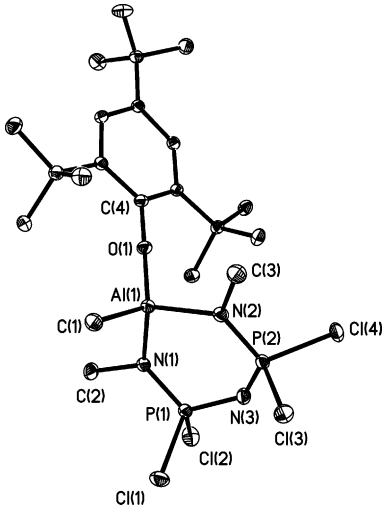
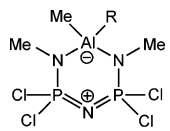


Figure 4. Molecular structure of **12** with thermal ellipsoids at the 50% probability level. Hydrogen atoms omitted. Selected bond lengths [Å] and angles [deg]: Al(1)−C(1), 1.956(2); Al(1)−O(1), 1.712(1), Al(1)−N(1), 1.918(2); Al(1)−N(2), 1.921(2); N(1)−P(1), 1.572(2); P(1)−N(2), 1.570(2); P(2)−N(1), 1.575(2); P(2)−N(3), 1.559(2); O(1)−C(4), 1.362(2); Al(1)−O(1)−C(4), 175.0(1); O(1)−Al(1)−C(1), 120.5(1); N(1)−Al(1)−N(2), 103.7(8); Al(1)−N(1)−P(1), 122.9(1); N(1)−P(1)−N(3), 114.9(1); P(1)−N(3)−P(2), 127.6(1); N(3)−P(2)−N(2), 115.6(1); P(2)−N(2)−Al(1), 124.9(1).

resonance at δ = 24.0 ppm was observed in the ^{31}P NMR spectrum of the reaction mixture. The ^{1}H NMR spectrum of the isolated product displayed the anticipated signals for the Mes*O group with the ^{t}Bu groups appearing as a set of singlet resonances (δ = 1.33 and 1.46 ppm for the para and ortho groups, respectively), with the aromatic protons resonating at δ = 7.28 ppm. Additional signals belonging to N−Me and Al−Me methyl protons were located at δ = 2.83 (m) and −0.46 (s) ppm, respectively. The successful preparation of the monosubstituted aluminatophosphazene $N(PCl_2NMe)_2AlMe(OMes^*)$ (**12**) was confirmed by a single-crystal X-ray diffraction study (Figure 4).

In a similar vein, a clean reaction was observed between $LiN(SiMe_3)_2$ and **5** to give the silylated amide derivative $N(PCl_2NMe)_2AlMe[N(SiMe_3)_2]$ (**13**) as a colorless oil. Compound **13** gave a downfield ^{31}P NMR signal (δ = 21.3 ppm) compared to that for **5** (δ = 23.6 ppm), and signals attributable to the $SiMe_3$, Al−Me and N−Me groups were observed in the anticipated integration ratio by ^{1}H NMR. A 1:1 stoichiometric reaction of MeLi with **5** cleanly yielded the methylated analogue **6**. This route proved to be advantageous over the previously discussed methylation strategy involving the reaction of **5** with excess $AlMe_3$, as purification of **6** was rendered much simpler. Using a similar strategy, the ethyl-substituted derivative $N(PCl_2NMe)_2AlMeEt$ (**14**)



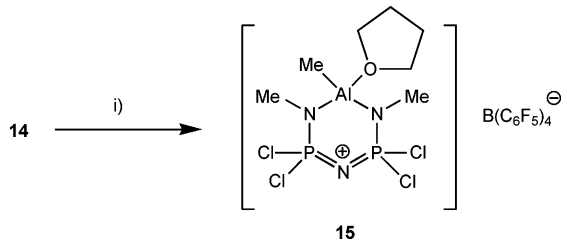
12 R = OMes*
13 R = $N(SiMe_3)_2$
14 R = Et

was readily prepared from EtMgCl and **5** and was obtained

as a colorless oil.[30] The ^{1}H and ^{13}C{^{1}H} NMR spectra of **14** were quite similar to those observed for the related tetramethylated aluminatophosphazene **6** except for the presence of the expected additional resonances arising from the ethyl group.

Isolation of the Alumazine−Phosphazene Hybrid Cation [N(PCl$_2$NMe)$_2$AlMe·THF]$^+$, [7·THF]$^+$. The generation of cationic aluminum complexes by the interaction of alkylated aluminum centers with the methide abstractors $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ has been reported.[2,31] Our investigations in this regard began with a study of the reactivity of **5** toward the methyl abstractor, $B(C_6F_5)_3$. The reaction was monitored by NMR (in CD_2Cl_2), and evidence for rapid (<20 min) methyl abstraction from the aluminum center was observed as the formation of the contact-free $[MeB(C_6F_5)_3]^-$ anion was detected by ^{1}H [$\delta = 0.45$ (s) ppm] and ^{19}F [$\delta = -133.2$ (br), -165.5 (t), and -167.7 (t) ppm] NMR spectroscopy.[32] However, we also observed simultaneous Me/C_6F_5 exchange, presumably between the initially formed cationic aluminum species **[7]**$^+$ and the $[MeB(C_6F_5)_3]^-$ counterion, as the methylated borane, $MeB(C_6F_5)_2$ [^{1}H NMR: $\delta = 1.70$ (s) ppm], was also present in the reaction mixture.[33] Consistent with the formation of a complicated mixture of products was the observation of many signals (>20) in the ^{19}F NMR spectrum and the appearance of a series of downfield-shifted ^{31}P NMR resonances ($\delta = 25-27$ ppm) due to the generation of either cationic and/or C_6F_5-substituted aluminum centers. The abstraction of a perfluorophenyl ring from the generally unreactive $[MeB(C_6F_5)_3]^-$ anion has been observed previously in related cationic aluminum systems[34] and suggests that the initial formation of the desired cation, **[7]**$^+$, did occur. However, the high reactivity of this species resulted in an undesired functional group scrambling reaction with the counterion.

Scheme 3. Preparation of the Cationic Aluminatophosphazene **[7·THF]**$^+$[a]



[a] (i) $Ph_3C[B(C_6F_5)_4]$, THF (1 equiv), CH_2Cl_2, 30 min.

We were encouraged by recent reports by Lappert[31b] and Gibson[35] concerning the use of coordinating THF to stabilize highly reactive cationic aluminum centers. Compound **14** was reacted with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in the presence of THF (in CD_2Cl_2, 1 h). Analysis of the resulting yellow solution by ^{31}P NMR revealed a single resonance at $\delta = 27.3$ ppm which was considerably downfield-shifted from the ^{31}P NMR resonance of the starting material, **14** ($\delta = 20.2$ ppm). The ^{19}F NMR spectrum was also clean, with the $[B(C_6F_5)_4]^-$ counterion as the sole detectable fluorinated species. The ^{1}H NMR spectrum indicated that the complete conversion of the $[Ph_3C]^+$ cation [$\delta = 7.66$ (d), 7.88 (t), and 8.27 ppm (t)] to triphenylmethane, Ph_3CH [$\delta = 7.1-7.3$ (m, Ph) and 5.55 (s, CH) ppm] had taken place, and therefore, the desired β-hydride abstraction reaction involving the aluminum-bound ethyl group in **14** was successful. The signals associated with the presence of an Al−Et moiety were no longer present, and a new Al−Me resonance was now detected at $\delta = -0.39$ ppm; by comparison, the ^{1}H NMR resonance (in CD_2Cl_2) of the Al−Me group in **14** occurs at $\delta = -0.70$ ppm. A molecule of THF was clearly coordinated to the aluminum center, as illustrated by the presence of a set of broad resonances at $\delta = 2.88$ and 4.23 ppm, which were located downfield relative to the ^{1}H NMR resonance of free THF [$\delta = 1.85$ and 3.76 ppm]. All of the above data convincingly support the formation the novel donor-stabilized alumazine−phosphazene hybrid cation $[N(PCl_2NMe)_2AlMe\cdot THF][B(C_6F_5)_4]$, **[7·THF]**$[B(C_6F_5)_4]$, (**15**) (Scheme 3). Removal of the Ph_3CH byproduct was accomplished by repeatedly washing the isolated orange oil with hexanes to give a yellow solid. Rigorous exclusion of moisture is required in order to prevent the hydrolysis of **15**, as evidenced by the appearance of a new ^{31}P NMR resonance at $\delta = 20.5$ ppm. Compound **15** can be stored in the solid state for indefinite periods of time in a glovebox freezer (−30 °C) without significant decomposition. All attempts to obtain a crystalline sample of **15** of suitable quality for single-crystal X-ray diffraction have been unsuccessful.[36] In addition, the continual presence of trace (ca. 5% by ^{1}H NMR) amounts of unidentified byproducts precluded the accurate characterization of **15** by elemental analysis.

(25) Rivard, E.; McWilliams, A. R.; Lough, A. J.; Manners, I. *Acta Crystallogr.* **2002**, *58C*, 114 and references therein.
(26) Kitashita, K.; Hagiwara, R.; Ito, Y.; Tamada, O. *Solid State Sci.* **2000**, *2*, 237.
(27) Klapötke, T. M. *J. Chem. Soc., Dalton Trans.* **1997**, 553.
(28) For salient discussions involving the nature of Al−O−C bonding, see: (a) Barron, A. R. *Polyhedron* **1995**, *22*, 3197. (b) Burford, N. *Coord. Chem. Rev.* **1992**, *112*, 1.
(29) An unusually short Al−O bond (1.659(3) Å) involving a tetracoordinate Al center has recently been reported. The exact nature of this bond is still under investigation: Neculai, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Walfort, B.; Stalke, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4294.
(30) Use of EtMgBr in THF cleanly produces **14** in situ (by ^{31}P NMR); however, the similar solubilities of the THF solvated MgBrCl byproduct and **14** prevented the isolation of the latter in pure form by this route. Pure **14** was alternatively obtained using a solution of EtMgCl in Et_2O as the ethylating reagent.
(31) For cationic aluminum heterocycles, see: (a) Radzewicz, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384. (b) Coslédan, F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 705. (c) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274. (d) Cameron, P. A.; Gibson, V. C.; Redsahw, C.; Segal, J. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 415. (e) Schmidt, J. A. R.; Arnold, J. *Organometallics* **2002**, *21*, 2306.
(32) Klosin, J.; Roof, G. R.; Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684.
(33) Spitzmesser, S. K.; Gibson, V. C. *J. Organomet. Chem.* **2003**, *673*, 95.
(34) (a) Pappalardo, D.; Tedesco, C.; Pellecchia, C. *Eur. J. Inorg. Chem.* **2002**, 621. (b) see refs 18 and 33.
(35) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1472.
(36) Salts containing the $[B(C_6F_5)_4]^-$ anion are notoriously difficult to crystallize as they tend to form "clathrate"-type oils.

Table 1. Crystallographic Data and Structure Refinement for **5**, **11**, and **12**[a]

	5	**11**	**12**
formula	$C_3H_9Al_1Cl_5N_3P_2$	$C_2H_6Cl_4F_4N_3P_3$	$C_{21}H_{38}Al_1Cl_4N_3O_1P_2$
fw	353.30	382.81	579.26
crystal color and habit	colorless block	colorless rod	colorless block
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.6405(6)	6.3250(1)	10.2001(2)
b (Å)	7.8844(5)	12.2720(3)	14.9237(3)
c (Å)	19.100(1)	15.9610(4)	18.8602(3)
α (°)	90	90	90
β (°)	105.851(3)	96.027(1)	97.967(1)
γ (°)	90	90	90
V (Å^3)	1415.4(2)	1232.1(1)	2843.3(1)
Z	4	4	4
$\rho_{(calc)}$ (g/cm)	1.658	2.064	1.353
μ (mm^{-1})	1.282	1.374	0.579
cryst size	0.40 × 0.30 × 0.30	0.28 × 0.23 × 0.20	0.35 × 0.35 × 0.32
θ range (°)	2.72−27.53	2.57−27.44	2.57−27.55
total reflns	3433	9415	35 483
	$R_{int} = 0.0220$	$R_{int} = 0.0447$	$R_{int} = 0.0440$
independent reflns	3200	2788	6539
R1[b] ($I > 2\sigma(I)$)	0.0365	0.0353	0.0354
wR2[c] (all data)	0.0795	0.0866	0.0903

[a] Data collection temperature 150(1) K. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Single-Crystal X-Ray Diffraction Studies of Cyclic Heterophosphazenes 5, 11, and 12. The crystallographic data for compounds **5**, **11**, and **12** are summarized in Table 1. In the solid state, aluminatophosphazene **5** adopts a boat conformation with the aluminum atom and two coordinate nitrogen atom [N(2)] displaced 0.532(2) and 0.265(2) Å above the remaining P_2N_2 plane (Figure 1). The aluminum center has a distorted tetrahedral geometry with identical Al−N bond lengths of 1.889(2) Å and are of similar value as typical Al−N single bonds within four-coordinate aluminum complexes.[15] The P−N bond lengths within **5** vary from the short bonds involving N(2) [1.563(2) Å avg] to the slightly longer P−N bonds involving the methylated nitrogen atoms N(1) and N(3) [1.575(2) avg]; these bond distances are considerably shorter than those of typical P−N single bonds (1.69−1.72 Å)[16] and suggest some multiple-bond character is present within **5**. The axially positioned Al−Cl bond appeared to be somewhat elongated [2.161(1) Å] when compared to the Al−Cl distances within most four-coordinate aluminum species (e.g., Al−Cl lengths within the $AlCl_4^-$ anion usually range from 2.12 to 2.14 Å).

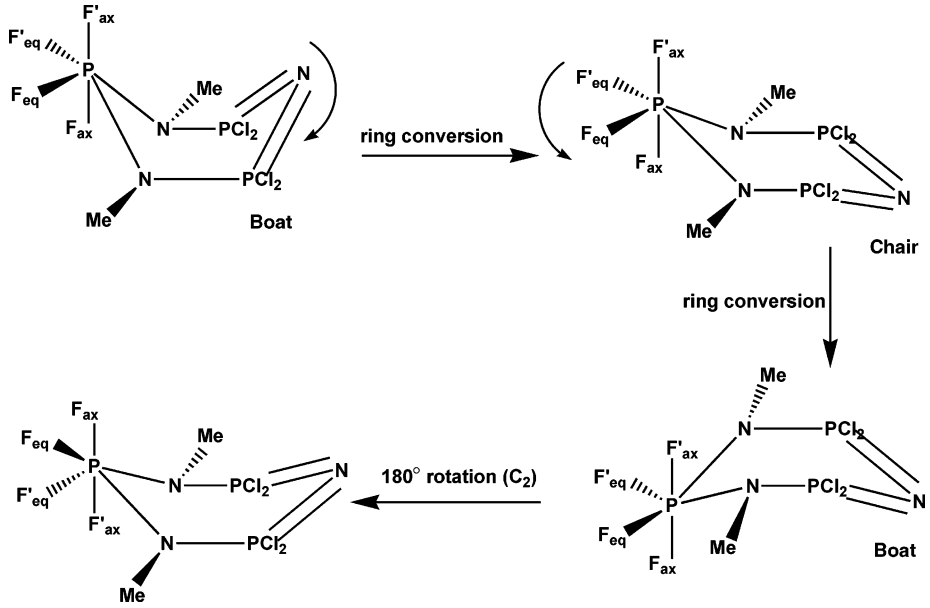
As shown in Figure 3, the zwitterionic phosphazene heterocycle **11** also adopts a boat conformation, with the formally anionic phosphorus atom [P(1)] lying considerably above the plane created by the central P−N ring atoms [0.84(2) Å]; the two-coordinate nitrogen atom [N(3)] is also buckled away from the internal P_2N_2 plane and resides at a distance of 0.29(2) Å above this plane. The geometry about P(1) is very close to a perfect octahedron, with an axial F(3)−P(1)−F(4) bond angle of 179.2(1)° and adjacent F−P−F angles all close to 90° (range from 89.4(1)° to 90.8(1)°). Furthermore, the equatorial fluorine [F(1) and F(2)] and nitrogen [N(1) and N(2)] atoms are also coplanar (equatorial angle sum about P(1): 360.0(2)°) with a N(1)−P(1)−N(2) bite angle of 92.4(1)°. The P−N bond lengths within **11** vary considerably with the longest P−N bonds involving the hexacoordinate P(1) (1.816(2) Å avg), while the remaining phosphorus atoms [P(2) and P(3)] form much shorter bonds with the neighboring nitrogen atoms (range from 1.561(2) to 1.603(2) Å). The shorter P−N bonds suggest some π-bonding occurs within the P_2N_3 unit as these P−N distances approach those within the $[Cl_3P{=}N{=}PCl_3]^+$ cation (1.51−1.56 Å).[25] The elongated P−N bonds involving P(1) are of similar length to those observed in related fluorinated phosphazene heterocycles (ca. 1.7−1.8 Å)[24a,b] and implies a weaker bonding interaction is present when compared to the remaining, shorter, P−N bonds within the ring. The P−F bond distances within **11** are similar (1.597(2)−1.610(2) Å) and comparable to those within PF_6^-.[26]

Heterocycle **12** exists in a twist chair conformation with a distorted tetrahedral aluminum center (Figure 4). The internal heterocyclic N(1)−Al−N(2) angle is 103.7(2)°, and an almost linear Al−O−C(Mes*) angle of 175.0(1)° is observed. The presence of such a wide Al−O−C angle is not surprising, as this unit has been known to adopt angles from 130° to near 180°, and this effect has been explained in terms of a low energy barrier required to deform the Al−O−C unit, rather than the presence of π-bonding; thus, crystal packing forces largely dictate which geometry is adopted in the solid state.[28] Consistent with the above explanation, the Al−O and C−O bond distances within **12** (1.712(2) and 1.362(2) Å, respectively) show little multiple-bond character and compare well with established values for single bonds.[29] The Al−N (1.918(2) and 1.921(2) Å) and P−N distances within **12** (1.559(2)−1.575(2) Å) are similar to those observed in the precursor, **5**; thus, the bonding within the aluminatophosphazene ring framework appears to be largely insensitive to the nature of the substitutents at the aluminum center.

Fluxionality of the Zwitterionic Phosphazene (11) Probed by Variable-Temperature ^{19}F NMR Spectroscopy. The ^{19}F NMR of **11** in CD_2Cl_2 at room temperature consisted of one set of resolved signals centered at $\delta = -65.5$ ppm (doublet of triplets), accompanied by significantly broadened resonances centered at $\delta = -25$ and -68 ppm.

As broadened signals have been observed in the room temperature ^{19}F NMR spectrum of the related arsenic heterocycle, $N(PCl_2NMe)_2AsF_4$ (**3**),[9] we decided to perform a variable-temperature NMR study on **11** in order to better understand its behavior in solution. Upon cooling the sample, progressive sharpening of the signals was observed until three sets of well-defined resonances (1:2:1 integration ratio) could be discerned (Figure 5). On the basis of the ^{19}F NMR spectrum of the arsenic analogue, we assigned the doublet of triplets at $\delta = -26.0$ ppm to the axial fluorine F(3) atom ($^1J_{FP} = 776$ Hz; $^2J_{FF}$ (cis) = 55.0 Hz; no trans F−F coupling was observed).[27] The doublet of triplets at $\delta = -64.6$ ppm ($^1J_{FP} = 815$ Hz; $^2J_{FF}$ (cis) = 56.9 Hz) was subsequently assigned to the equatorial fluorine atoms [F(1) and F(2)] on the basis of the observed integration ratio. Surprisingly, the resonance due to the remaining axial fluorine atom F(4) ($\delta = -68.2$ ppm) displayed a complex doublet of multiplets ($^1J_{FP} = 812$ Hz). This complex resonance suggests further

Scheme 4. Proposed Pathway for Ring Fluxionality (Boat−Chair−Boat) within **11**



coupling between this atom and two magnetically inequivalent phosphorus atoms within the phosphazene ring occurs due to the closer proximity of F(4) compared to F(3) (assuming that no trans F−F coupling occurs). Above −40 °C, the resonances due to the axial F atoms broaden, presumably due to a ring inversion process (Scheme 4) which exchanges the positions of the axial fluorine atoms, while the equatorial F atoms remain in a similar chemical environment throughout the ring inversion; thus, the resonances associated with the equatorial fluorine atoms (dt, $\delta = -64.6$ ppm) remain unchanged during the course of the variable-temperature experiment. At room temperature, the resonances due to the axial fluorine atoms are still discernible (yet broad), indicating that the exchange process is still slow on the NMR time scale.

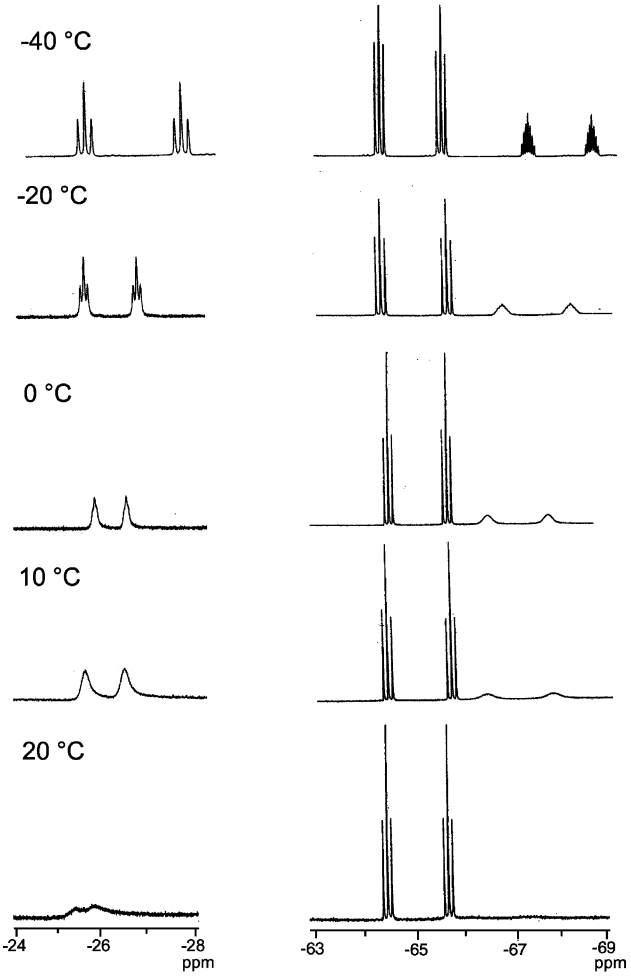


Figure 5. Variable-temperature ^{19}F NMR spectra of compound **11** in CD_2Cl_2.

Conclusions

The aluminum-containing heterophosphazene $N(PCl_2NMe)_2AlMeCl$ (**5**) has been prepared via a rare skeletal transmetalation reaction involving the boratophosphazene $N(PCl_2NMe)_2BCl_2$ (**1**) and $AlMe_3$. The successful synthesis of methylated **6** and chlorinated derivatives **8** was also achieved. A series of halide replacement reactions involving **5** and various nucleophiles was described, and in all cases, selective replacement of the aluminum-bound chlorine atom transpired. Treatment of **5** with $Ag[BF_4]$ and $Ag[PF_6]$ resulted in novel skeletal substitution reactions, whereby the aluminum atom was replaced by boron and phosphorus to give the fluorinated heterophosphazenes **10** and **11**, respectively. Heterocycle **11** represents the first structurally characterized zwitterionic phosphazene ring, and the fluxionality of **11** in solution was studied using variable-temperature ^{19}F NMR spectroscopy. Furthermore, the preparation of the first example of a stable alumazine−phosphazene hybrid cation $[N(PCl_2NMe)_2AlMe{\cdot}THF]^+$, **[7·THF]**$^+$, was described. This species and its analogues are possible candidates for catalysis and as precursors to novel inorganic polymers via ROP strategies.

Experimental Section

General. All reactions and manipulations were carried out strictly under an atmosphere of prepurified argon or nitrogen (BOC) using

either Schlenk techniques or an inert-atmosphere glovebox (M-Braun). Solvents were dried and collected using a Grubbs-type[37] solvent system manufactured by M-Braun. ^{1}H NMR spectra were obtained on a Varian Gemini 300 spectrometer (300.1 MHz) and referenced to *protio* impurities in the NMR solvent. ^{11}B, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR spectra were also obtained using a Varian Gemini 300 spectrometer (96.0, 75.5, 282.2, and 121.5 MHz respectively) and were referenced externally to BF_3·OEt_2, $SiMe_4$ (TMS), $CFCl_3$/$CDCl_3$, and 85% H_3PO_4 in either $CDCl_3$, CD_2Cl_2, or D_2O (insert). Variable-temperature ^{19}F NMR spectra were recorded on a Varian Unity 500 spectrometer (470.2 MHz). Mass spectra were obtained with the use of a VG 70-250S mass spectrometer using a 70 eV electron impact ionization source. Elemental analyses were performed either by Quantitative Technologies, Inc., Whitehouse, NJ, or at the University of Toronto using a Perkin-Elmer Series 2400 CHN Analyzer. $GaCl_3$ and $AlCl_3$ were purchased from Aldrich and sublimed prior to use. $TaCl_5$ was obtained from Strem and sublimed prior to use. SO_2Cl_2 (BDH) was distilled under an atmosphere of nitrogen within 24 h of being used. BCl_3 (1.0 M solution in hexanes), $AlMe_3$ (2.0 M solution of toluene), EtMgCl (2.0 M solution in diethyl ether), $LiN(SiMe_3)_2$, and $B(C_6F_5)_3$ were also purchased from Aldrich and used as received. $Ag[OSO_2CF_3]$ (Aldrich), $Ag[BF_4]$ (Aldrich), and $Ag[PF_6]$ (Aldrich) were dried in vacuo (ca. 120 °C, 10^{-3} mmHg) prior to use. Boratophosphazene **1** was prepared according to a literature procedure[9] and was purified by recrystallization from a 1:1 CH_2Cl_2/hexanes mixture at −30 °C. 2,4,6-^{t}Bu$_3$C$_6$H$_2$OLi·OEt_2 (Mes*OLi·OEt_2)[38] and $[Ph_3C][B(C_6F_5)_4]$[2b] were prepared according to literature procedures.

X-Ray Crystallography. Diffraction data were collected on a Nonius Kappa-CCD difractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A combination of 1° ϕ and ω (with κ offsets) scans were integrated and scaled using the Denzo-SMN package.[39] The structures were solved and refined with the SHELXTL-PC v6.12 software package.[40] Refinement was by full-matrix least squares on F^2 using data (including negative intensities) with hydrogen atoms bonded to carbon atoms included in calculated positions and treated as riding atoms. The methyl groups within **11** were disordered and modeled with a 50/50 occupancy related by a 60° rotation about the N−C bond axis.

Preparative Details. Preparation of $N(PCl_2NMe)_2AlClMe$ (**5**). $AlMe_3$ (10.3 mL, 20.6 mmol, 2.0 M solution in toluene) was added dropwise to **1** (3.66 g, 10.2 mmol) in 100 mL of toluene at 0 °C to give a colorless solution. The mixture was allowed to warm to room temperature and stirred for 5 h; removal of the volatiles in vacuo afforded a white residue. Recrystallization from toluene (2 mL, −30 °C, 12 h) produced large colorless blocks of **5** (2.14 g, 59%).

^{1}H NMR ($CDCl_3$): $\delta = -0.57$ (s, Al−Me, 3H) and 2.85 (m, N−Me, 6H). ^{11}B NMR ($CDCl_3$): no signal detected. ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 31.1$ (m, N−Me); no Al−Me resonance was observed. ^{31}P NMR ($CDCl_3$): $\delta = 23.6$ (s). MS EI, 70 eV (*m*/*z*, %): 355 ($M^+ + 2H$, 20), 338 ($M^+ - Me$, 5), 319 ($M^+ - Cl$, 100). Anal. Calcd for $C_3H_9Al_1Cl_5N_3P_2$: C, 10.20; H, 2.57; N, 11.89. Found: C, 9.58; H, 2.43; N, 11.51.

Preparation of $N(PCl_2NMe)_2AlMe_2$ (**6**). A solution of $AlMe_3$ (0.60 mL, 1.2 mmol, 2.0 M solution in toluene) was added dropwise to a colorless solution of **5** (0.20 g, 0.56 mmol) in 15 mL of toluene at 0 °C. After the reaction was warmed to room temperature and stirred for 3 h, the solvent was removed in vacuo, leaving a colorless oil that gradually solidified into a waxy white solid (0.15 g, 80%). ^{1}H NMR ($CDCl_3$): $\delta = -0.82$ (s, Al−Me, 6H) and 2.76 (m, N−Me, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = -10.6$ (br, Al−Me) and 31.0 (m, N−Me). ^{31}P NMR ($CDCl_3$): $\delta = 21.5$ (s). MS EI (70 ev, *m*/*z*, %): 318 ($M^+ - Me$, 13), 298 ($M^+ - Cl$, 5), 283 ($M^+ - Me - Cl$, 1), 262 ($M^+ - 2Cl$, 5), 227 ($M^+ - 3Cl$, 2). Anal. Calcd for $C_4H_{12}Al_1Cl_4N_3P_3$: C, 14.43; H, 3.63; N, 12.62. Found: C, 14.79; H, 3.58; N, 11.81.

Alternatively, MeLi (1.6 M solution in Et_2O, 0.90 mL, 1.4 mmol) was added dropwise to a solution of **5** (0.50 g, 1.4 mmol) in toluene at −78 °C. The reaction was warmed to room temperature and stirred for 16 h to give a cloudy mixture. Filtration followed by removal of the volatiles gave a colorless oil that slowly solidified to a white solid which gave identical NMR data as that reported above (0.33 g, 70%).

Preparation of $N(PCl_2NMe)_2AlCl_2$ (**8**). A solution of $GaCl_3$ (0.14 g, 0.80 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a solution of **5** (0.27 g, 0.76 mmol) in 10 mL of CH_2Cl_2 at room temperature. After 8 h, the volatiles were then removed from the colorless solution to give a white powder, which was recrystallized from a 1:1 hexanes/CH_2Cl_2 mixture (−30 °C, 24 h) to give colorless blocks (0.28 g, 98%).

^{1}H NMR ($CDCl_3$): $\delta = 2.92$ (m, N−Me). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 31.2$ (m, N-Me). ^{31}P NMR ($CDCl_3$): $\delta = 25.3$ (s). MS EI, 70 eV (*m*/*z*, %): 373 (M^+, 87), 338 ($M^+ - Cl$, 80), 288 ($M^+ - 2Cl - Me$, 88). Anal. Calcd for $C_2H_6Al_1Cl_6N_3P_2$: C, 6.43; H, 1.62. N, 11.24. Found: C, 6.24; H, 1.69; N, 10.74.

Preparation of $N(PCl_2NMe)_2AlMe(OSO_2CF_3)$ (**9**). In the absence of light, **5** (0.26 g, 0.73 mmol) in 2 mL of CH_2Cl_2 was added to a suspension of $Ag[OSO_2CF_3]$ (0.20 g, 0.79 mmol) in 5 mL of CH_2Cl_2. The immediate formation of a pale purple precipitate was observed, and the reaction was stirred for 16 h. Filtration of this mixture followed by removal of the volatiles in vacuo gave a colorless oil (0.29 g, 85%).

^{1}H NMR ($CDCl_3$): $\delta = -0.52$ (s, Al−Me, 3H) and 2.86 (m, N−Me, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = -15.1$ (br, Al−Me), 31.1 (s, N−Me) and 118.9 (q, $^1J_{CF} = 316$ Hz, OSO_2CF_3). ^{19}F NMR ($CDCl_3$): $\delta = -77.6$ (s). ^{31}P NMR ($CDCl_3$): $\delta = 25.7$ (s).

Preparation of $N(PCl_2NMe)_2BF_2$ (**10**) from the Reaction of **5** with $Ag[BF_4]$. In the absence of light, **5** (0.094 g, 0.27 mmol) in 1 mL of CH_2Cl_2 was added to a suspension of $Ag[BF_4]$ (0.054 g, 0.28 mmol) in 3 mL of CH_2Cl_2. The immediate formation of a white precipitate was observed, and the reaction was stirred for 16 h. The mixture was filtered, and removal of the volatiles provided a white solid (0.050 g, 58%), which was identified as **10** on the basis of NMR spectroscopy.[9]

^{1}H NMR ($CDCl_3$): $\delta = 2.85$ (m, N−Me). ^{11}B NMR ($CDCl_3$): $\delta = 0.06$ (s). ^{19}F NMR ($CDCl_3$): $\delta = -147.5$ (m). ^{31}P NMR ($CDCl_3$): $\delta = 28.8$ (pseudoquartet). MS EI, 70 eV (*m*/*z*, %): 324 ($M^+ - H$, 26), 288 ($M^+ - 2F$, 15), 259 ($M^+ - BF_2Me$, 26).

Preparation of $N(PCl_2NMe)_2PF_4$ (**11**). In the absence of light, a solution of **5** (0.34 g, 0.96 mmol) in 1 mL of CH_2Cl_2 was added to a suspension of $Ag[PF_6]$ (0.25 g, 0.99 mmol) in 10 mL of CH_2Cl_2. The immediate formation of a pale purple precipitate was observed, and the reaction was stirred for 16 h. Filtration of this mixture afforded a pale yellow solution from which a light beige solid was isolated when the volatiles were removed in vacuo (0.21 g, 56%). Crystals (large colorless rods) suitable for single-crystal X-ray diffraction were obtained from a toluene solution at −30 °C (2 weeks).

(37) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(38) Bartlett, R. A.; Rasika Dias, H. V.; Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 5699.
(39) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.
(40) Sheldrick, G. M. SHELXTL-Windows NT. V.6.12, Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.

^{1}H NMR ($CDCl_3$): δ = 2.82 (m, N−Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 34.0 (s). ^{19}F NMR (470.2 MHz, CD_2Cl_2, −80 °C): δ = −26.0 (dt, F(3)-axial, $^1J_{FP}$ = 776 Hz; $^2J_{FF}$(cis) = 55.0 Hz), −64.6 (dt, F(1,2)-equatorial, $^1J_{FP}$ = 815 Hz; $^2J_{FF}$(cis) = 56.9 Hz), and −68.2 (dm, F(4)-axial, $^1J_{FP}$ = 812 Hz). ^{31}P NMR ($CDCl_3$, 20 °C): δ = 33.8 (d, PCl_2, $^2J_{PP}$ = 40 Hz) and −149.0 (ttt, PF_4, $^1J_{PF}$ (equatorial) = ∼800 Hz; $^1J_{PF}$ (axial) = ∼765 Hz; $^2J_{PP}$ = 41 Hz). MS EI, 70 eV (*m*/*z*, %): 382 (M^+ − H, 7), 364 (M^+ − F, 20), 346 (M^+ − 2F, 10), 276 (M^+ − PF_4, 45), 107 (PF_4^+, 90). Anal. Calcd for $C_2H_6Cl_4F_4N_3P_3$: C, 6.27; H, 1.58; N, 10.98. Found: C, 6.41; H, 1.50; N, 10.99.

Preparation of $N(PCl_2NMe)_2AlMe(OMes^*)$ (**12**). A solution of Mes*OLi·(OEt_2) (0.35 g, 1.0 mmol) in 5 mL of toluene was added to a solution of **5** (0.35 g, 0.99 mmol) in 5 mL of toluene. After 16 h, a white slurry was observed. Filtration of the mixture followed by removal of the volatiles gave a white solid, which was recrystallized from toluene (−30 °C, 16 h) to give large colorless blocks of **12** (0.36 g, 62%).

^{1}H NMR ($CDCl_3$): δ = −0.46 (s, Al−Me, 3H), 1.33 (s, *para*-^{t}Bu (Mes*O), 9H), 1.46 (s, *ortho*-^{t}Bu (Mes*O), 18H), 2.83 (m, N−Me, 6H), and 7.28 (s, Ar−H (Mes*O), 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 (s, ^{t}Bu), 31.5 (br, N−Me), 32.0 (s, ^{t}Bu), 34.6 (s, ^{t}Bu), 35.4 (s, ^{t}Bu), 122.5 (s, C_{aryl}), 137.9 (s, C_{aryl}), 139.1 (s, C_{aryl}), and 153.8 (s, C_{aryl}); no Al−Me resonance was observed. ^{31}P NMR ($CDCl_3$): δ = 24.0 (s). MS EI, 70 eV (*m*/*z*, %): 544 (M^+ − Cl, 3), 320 (M^+ − Mes*OH, 36), 262 (Mes*OH, 17), 247 (Mes*OH − Me, 100). Anal. Calcd for $C_{21}H_{38}Al_1Cl_4N_3O_1P_2$: C, 43.54; H, 6.61; N, 7.25. Found: C, 44.02; H, 6.91; N, 7.09.

Preparation of $N(PCl_2NMe)_2AlMe[N(SiMe_3)_2]$ (**13**). A pale yellow solution of $LiN(SiMe_3)_2$ (0.17 g, 1.0 mmol) in 1 mL of toluene was added dropwise to a solution of **5** (0.35 g, 0.99 mmol) in 5 mL of toluene. The reaction was stirred for 16 h and filtered to give a colorless solution. Removal of the volatiles afforded a colorless oil (0.30 g, 65%).

^{1}H NMR ($CDCl_3$): δ = −0.69 (s, Al−Me, 3H), 0.14 (s, $N(SiMe_3)_2$, 18H), and 2.81 (m, N−Me, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 5.54 (s, $SiMe_3$) and 30.8 (br, N-Me); no Al−Me resonance was observed. ^{31}P NMR ($CDCl_3$): δ = 21.3 (s). MS EI, 70 ev (*m*/*z*, %): 314 (M^+ − $HN(SiMe_3)_2$, 35), 260 (M^+ − 2ClSiMe_3, 20).

Preparation of $N(PCl_2NMe)_2AlMeEt$ (**14**). To a solution of **5** (0.95 g, 2.7 mmol) in 20 mL of toluene was added dropwise a solution of EtMgCl (2.0 M solution in Et_2O, 1.35 mL, 2.7 mmol) at ambient temperature. Upon the addition of the Grignard reagent, a white suspension was observed. The reaction was stirred for 5 h, and filtration of the mixture gave a colorless solution. A colorless oil was obtained after the volatiles were removed in vacuo (0.53 g, 57%).

^{1}H NMR ($CDCl_3$): δ = −0.81 (s, Al−Me, 3H), −0.14 (q, $^3J_{HH}$ = 8.1 Hz, Al−CH_2−CH_3, 2H), 0.99 (t, $^3J_{HH}$ = 8.1 Hz, Al−CH_2−CH_3, 3H), and 2.80 (m, N-Me, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = −12.7 (v br, Al−*C*H_2−CH_3), −0.2 (br, Al−Me), 8.8 (s, Al−CH_2−*C*H_3), and 30.7 (m, N−Me). ^{31}P NMR ($CDCl_3$): δ = 20.2 (s). MS EI, 70 eV (*m*/*z*, %): 318 (M^+ − Et, 318, 45), 304 (M^+ − Et − Me, 10), 282 (M^+ − Et − Cl, 5). Anal. Calcd for $C_5H_{14}Al_1Cl_4N_3P_2$: C, 17.31; H, 4.07; N, 12.11. Found: C, 16.51; H, 4.10; N, 11.61.

Preparation of $[N(PCl_2NMe)_2AlMe{\cdot}THF][B(C_6F_5)_4]$ (**15**). Aluminatophosphazene **14** (28 mg, 0.081 mmol) and THF (6.5 mg, 0.090 mmol) were dissolved in 0.5 mL of CD_2Cl_2, and this solution was then added quickly to $[Ph_3C][B(C_6F_5)_4]$ (75 mg, 0.081 mmol) in 0.5 mL of CD_2Cl_2. After 1 h, the volatiles from the resulting bright yellow solution were removed to afford an orange oil. The residue was washed with hexanes (2 × 10 mL) and dried in vacuo to give a bright yellow solid (54 mg, 62%). ^{1}H NMR (CD_2Cl_2): δ = −0.39 (s, Al−Me, 3H), 2.17 (br, CH_2−CH_2−O, 4H), 2.88 (m, N-Me, 6H), 4.23 (br, CH_2−CH_2−O, 4H). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): −16.2 (br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 13.9 (s, Al-Me), 25.4 (s, *C*H_2−CH_2−O), 31.6 (s, N-Me), and 73.9 (s, CH_2−*C*H_2−O). ^{19}F NMR (CD_2Cl_2): −133.0 (br, 8F, *ortho*-C_6F_5), −163.5 (t, $^3J_{FF}$ = 20.5, 4F, *para*-C_6F_5), and −167.4 (t, $^3J_{FF}$ = 17.8, 8F, *meta*-C_6F_5). ^{31}P NMR (CD_2Cl_2): δ = 27.3 (s). Despite numerous attempts to purify **15**, material of purity greater than 95% could not be obtained (by ^{1}H NMR), thus precluding accurate elemental analysis.

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Supporting Information Available: X-ray crystallographic structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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