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Synthesis and Characterization of New Nitrogen-Donor-Stabilized *N*-Silylphosphoranimine Cations

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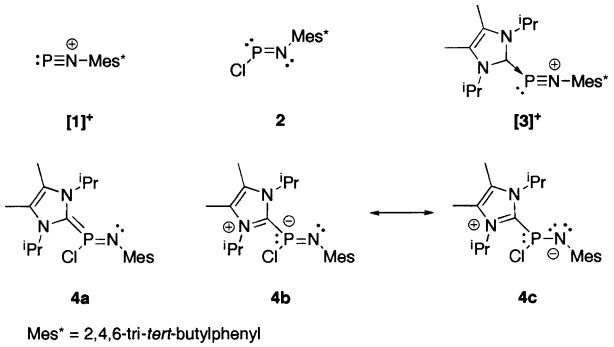
The phosphoranimine $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**12**) reacts quantitatively with nitrogen bases pyridine, 4,4′-bipyridine, and quinuclidine (quin) to form the *N*-donor stabilized phosphoranimine cations [*N*-donor·$P(OCH_2CF_3)_2{=}NSiMe_3$] (**[15]**$^+$) in the presence of the halide abstractor AgOTf. In contrast to quinuclidine, in the absence of a halide abstractor, the weak bases pyridine and 4,4′-bipyridine do not undergo reactions with **12** or with the phosphoranimine $Cl_3P{=}NSiMe_3$ (**7**). Furthermore, unlike the weaker bases, quinuclidine also reacts with **7** to form the expected quinuclidine-stabilized phosphoranimine cation [quin·$PCl_2{=}NSiMe_3$]$^+$ (**[16]**$^+$) in the presence of AgOTf. However, in the absence of AgOTf, quinuclidine reacts with **7** to presumably yield the salt **[16]Cl**, which then undergoes a further quinuclidine ring-opening reaction to yield the cationic piperidyl-substituted phosphoranimine [(quin)CH_2-$CH_2C_5H_9N$–$PCl_2{=}NSiMe_3$]Cl (**[19]Cl**). Reactions involving **7** and **12** with other halide abstraction reagents, such as $GaCl_3$, are also described.

Introduction

The study of cationic phosphorus−nitrogen compounds has attracted much attention over the past two decades, as they provide routes to new bonding environments between phosphorus and nitrogen.[1−6] For example, Niecke and co-workers have reported the preparation of an iminophosphonium cation [P≡NMes*]$^+$ (**[1]**$^+$) (Mes = 2,4,6-tri-*tert*-butylphenyl) from halide abstraction from the phosphinimine ClP=NMes* (**2**). The cation **[1]**$^+$ provided the first example of a formal triple bond between phosphorus and nitrogen.[3] Also, Burford and co-workers have reported carbene-stabilized derivatives of **[1]**$^+$ and **2**, in the form of donor−acceptor complexes **[3]**$^+$ and **4**, respectively.[7,8] While



compound **4** can be represented as a trigonal planar phosphorus(V) species **4a**, the pyramidal geometry about phosphorus, as revealed from X-ray diffraction studies, clearly indicates the presence of a stereochemically active lone pair and thus best represented by resonance forms **4b** or **4c**. This type of iminophosphide (**4b**) or phosphinimide (**4c**) bonding environment is again unprecedented for phosphorus.

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(1) Regitz, M., Scherer, O. J., Eds. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Georg Thieme Verlag: New York, 1990.
(2) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.
(3) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715.
(4) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.
(5) Loss, S.; Widauer, C.; Grützmacher, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3329.
(6) Johnson, A. W. *Ylides and Imines of Phosphorus*; John Wiley and Sons: New York, 1993.
(7) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Phillips, A. D.; Concolino, T. E.; Lam, K.-C.; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 5413.
(8) Burford, N.; Dyker, S. A.; Phillips, A. D.; Spinney, H. A.; Decken, A.; McDonald, R.; Ragogna, P. J.; Rheingold, A. L. *Inorg. Chem.* **2004**, *43*, 7502.

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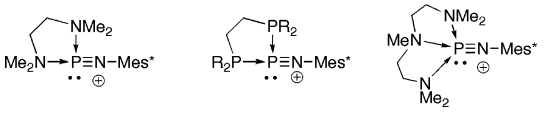
In addition to monodentate donors, the same group has reported bidentate nitrogen **[5a]**$^+$ and phosphorus **[5b]**$^+$



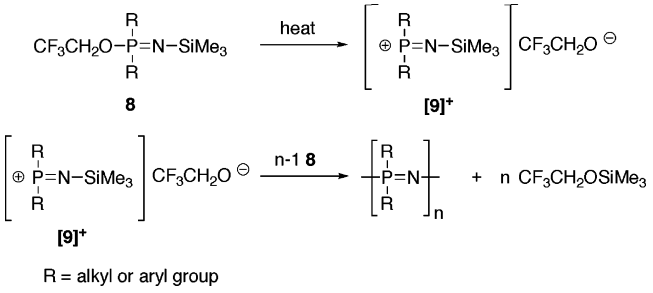
[5a]$^+$ **[5b]**$^+$ **[6]**$^+$

cationic derivatives of **2** as well as incorporating a tridentate nitrogen ligand (to give **[6]**$^+$) in this series of compounds.[9] The cations **[5]**$^+$ and **[6]**$^+$ formally represent hypercoordinate phosphorus(III) species and further support the ability of phosphorus(III) centers to act as Lewis acceptors while maintaining a stereochemically active lone pair of electrons.

Moreover, cationic phosphophosphorus(V)−nitrogen compounds have shown to play an integral role in phosphazene polymerization chemistry as reactive intermediates.[10] For example, the thermal ring-opening polymerization of the cyclic phosphazene trimer $[Cl_2P{=}N]_3$ is believed to proceed through the cationic intermediate $[Cl_5P_3N_3]^+$. The living cationic condensation polymerization of the *N*-silylphosphoranimine monomer $Cl_3P{=}NSiMe_3$ (**7**),[11] catalyzed by PCl_5, proceeds through the cationic initiator $[Cl_3P{=}N{=}PCl_3]^+$.[12−14] Cationic *N*-silylphosphoranimines are also of particular interest because they have been proposed to be the key intermediates in the thermal condensation polymerization of phosphoranimine monomers with the general formula $(F_3CCH_2O)R_2P{=}NSiMe_3$ (**8**) at ca. 180−200 °C.[15,16] Under these conditions it is believed that the *N*-silylphosphoranimine cation (**[9]**$^+$) is formed from initial ionization of the P−O bond in **8** (Scheme 1). The base-free cation **[9]**$^+$ is presumed to subsequently function as an initiator by inducing the chain-growth polymerization of the remaining phosphoranimine monomer.[17]

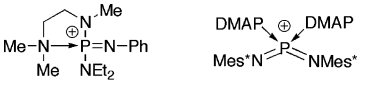
The coordinatively unsaturated phosphorus(V) center in **[9]**$^+$ makes this species very Lewis acidic and highly reactive. To render such species isolable, additional stabilization from neutral bases would likely be required and a few examples of donor-stabilized phosphorus(V)−nitrogen cations can be found in the current literature. For example, Schmutzler and co-workers have reported iminophosphonium salts which are intramolecularly stabilized by a pendant nitrogen

Scheme 1



R = alkyl or aryl group

donor, $[(NEt_2)((NMe_2)CH_2CH_2N(Me))P{=}N{-}Ph]^+$ (**[10]**$^+$),[18] and Niecke and co-workers have reported a bis DMAP



[10]$^+$ **[11]**$^+$

(4-dimethylaminopyridine) adduct of a bisiminophosphonium cation $[Mes^*N{=}P(DMAP)_2{=}NMes^*]^+$ (**[11]**$^+$).[19]

Our group has recently reported the synthesis and characterization of a series of DMAP-stabilized phosphoranimine cations ($[DMAP{\cdot}PR_2{=}NSiMe_3]X$; R = Cl, Me, Ph, OCH_2CF_3; X = Cl^-, Br^-, $OSO_2CF_3^-$).[20,21] These salts were formed from the reactions between the parent phosphoranimines $XR_2P{=}NSiMe_3$ and DMAP in the presence or absence of the halide-abstracting agent AgOTf (OTf = OSO_2CF_3). From this study, we have found an intimate relationship between cation stability and phosphoranimine substituent R and/or counteranion X, such that electron-withdrawing substituents (Cl and OCH_2CF_3) and weakly-coordinating ions (SbF_6^- and OTf^-) yield the most stable salts. Therefore, we were interested to examine the stability of the aforementioned phosphoranimine cations, where R = Cl or OCH_2CF_3, with respect to other nitrogen-based donors and halide-abstracting agents. In this paper we describe the reactions of the phosphoranimines **7** and $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**12**)[22] with the nitrogen donors pyridine, 4,4′-bipyridine, and quinuclidine (quin) in the presence or absence of AgOTf. Also, we describe the reactions of **7** and **12** solely with the halide-abstracting agents AgOTf, TMSOTf (TMS = Me_3Si), MeOTf, and $GaCl_3$ in the absence of a donor.

Experimental Section

General. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen or argon (Air Products) using common Schlenk techniques or an inert atmosphere glove box (M-Braun). Hexanes were dried and collected using a Grubbs-type solvent purification system manufactured by M-Braun.[23] CH_2Cl_2

(9) Burford, N.; Phillips, A. D.; Spinney, H. A.; Lumsden, M.; Werner-Zwanziger, U.; Ferguson, M. J.; McDonald, R. *J. Am. Chem. Soc.* **2005**, *127*, 3921.
(10) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; Wiley−Interscience: New York, 2003.
(11) (a) Wang, B.; Rivard, E.; Manners, I. *Inorg. Chem.* **2002**, *41*, 1690. (b) For the first report of this species, see: Niecke, E.; Bitter, W. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 127.
(12) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035.
(13) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1997**, *30*, 50.
(14) Rivard, E.; Lough, A. J.; Manners, I. *Inorg. Chem.* **2004**, *43*, 2765.
(15) Wisian−Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848.
(16) Neilson, R. H.; Hani, R.; Wisian−Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910.
(17) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.
(18) Becker, W.; Jones, P. G.; Schomburg, D.; Schmutzler, R. *Chem. Ber.* **1990**, *123*, 1759.
(19) Blättner, M.; Nieger, M.; Ruban, A.; Schoeller, W. W.; Niecke, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2768.
(20) Rivard, E.; Huynh, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 2286.
(21) Huynh, K.; Rivard, E.; Lough, A. J.; Manners, I. *Chem. Eur. J.* **2007**, *13*, 3431.
(22) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875.
(23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

was dried at reflux over CaH_2. Et_2O was dried at reflux over Na/benzophenone. ^1H, $^{13}C\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian Gemini 300 spectrometer (300.1, 75.4, 282.3, and 121.5 MHz) and were referenced either to protic impurities in the solvent (^1H) or externally to $SiMe_4$ ($^{13}C\{^1H\}$), $CFCl_3$ (^{19}F) in $CDCl_3$, $BF_3{\cdot}Et_2O$ (^{11}B), and 85% H_3PO_4 ($^{31}P\{^1H\}$) in $CDCl_3$. $^{29}Si\{^1H\}$ NMR spectra were obtained on a Varian Unity 400 spectrometer (79.4 MHz) and was referenced externally to $SiMe_4$ in $CDCl_3$. Mass spectra were obtained with the use of a VG-250S mass spectrometer using a 70 eV electron impact ionization source. Melting points (uncorrected) were obtained in 0.5 mm (o.d.) glass capillaries, which were flame-sealed under nitrogen. Elemental analyses were performed at the University of Toronto using a Perkin-Elmer 2400 Series CHN analyzer. Celite was dried in an oven at 120 °C for 24 h. PCl_3, SO_2Cl_2, and pyridine were distilled under N_2 and degassed prior to use. $LiN(SiMe_3)_2$, 4,4′-bipyridine, quin, methyl triflate, trimethylsilyl triflate, and $GaCl_3$ were purchased from Aldrich and used as received. The silver salt AgOTf was also obtained from Aldrich and dried under dynamic vacuum at 100 °C for 24 h prior to use. **12**[22] was prepared according to a literature procedure.

X-ray Structure Determination. Data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A combination of 1° ϕ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[24] The structures were solved and refined with the SHELXTL-PC v6.12 software package.[25] 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.

High-Yield Preparation of $Cl_3P{=}NSiMe_3$ (7). Lithium bis(trimethylsilyl)amide (55.4 g, 0.33 mol) was cooled to 0 °C, and Et_2O (900 mL) was transferred via cannulation. After a dropwise addition of PCl_3 (29.0 mL, 0.33 mol) over 30 min to the rapidly stirred suspension of $LiN(SiMe_3)_2$ at 0 °C, the resulting white suspension was allowed to stir for a further 60 min at 0 °C. Neat SO_2Cl_2 (26.6 mL, 0.33 mol) was added dropwise over 30 min at 0 °C. The off-white suspension was allowed to warm to ambient temperature and stirred for an additional 60 min. The white suspension was then filtered through a medium-porosity frit with a 1 cm pad of predried Celite via cannulation. Et_2O (100 mmHg, 20 °C) and Me_3SiCl (10 mmHg, 20 °C) were removed from the filtrate by fractional reduced-pressure distillation. The remaining liquid was then transferred, via syringe under N_2, to a new small volume trap-to-trap distillation apparatus, composed of a two-neck round-bottom flask (250 mL) equipped with a septum and a pear-shaped flask (250 mL) with a Schlenk attachment connected by a 20 cm glass distillation bridge. The septum was replaced with a glass stopper under a dynamic flow of N_2. The flask containing crude **7** was then frozen with liquid N_2, and the *entire* system was then placed under dynamic vacuum (0.01 mmHg, −196 °C) for 30 min. The dynamic vacuum applied to the distillation apparatus was then shut off, the pear-shaped flask was cooled with liquid N_2, and the flask containing crude **7** was allowed to warm and distill at 25 °C under *static* vacuum of ∼0.01 mmHg. It is important to note that the distillation may require occasional adjustments to the vacuum and the temperature of the flask containing crude **7** should be maintained at 25 °C. The distillation process may require up 90 min for a high yield (62 g, 84%) of pure **7** as a colorless and moisture-sensitive liquid (bp 24 °C, 0.2 mmHg). Spectroscopic data for **7** have previously been reported.[11a]

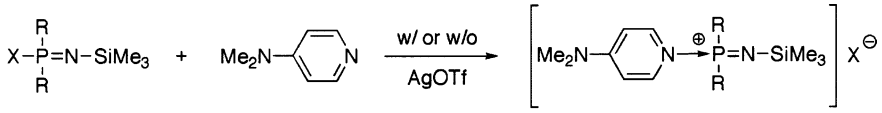
Preparation of [pyridine·$P(OCH_2CF_3)_2{=}NSiMe_3$]OTf ([15a]OTf). To a stirring suspension of pyridine (0.18 g, 2.24 mmol) and AgOTf (0.58 g, 2.24 mmol) in 5 mL of $CHCl_3$ was added a 5 mL $CHCl_3$ solution of **12** (0.89 g, 2.42 mmol). The resulting off-white suspension was stirred for 18 h and then filtered, yielding a yellow filtrate. All volatiles were removed from the filtrate and recrystallization of the crude yellow solid from a concentrated solution of CH_2Cl_2 by slow evaporation yielded clear colorless crystals of **[15a]OTf** (0.88 g, 72%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −24.9 ppm (s). ^1H NMR ($CDCl_3$): 0.21 (d, $^3J_{HP} = 0.9$ Hz, 9H, $SiMe_3$), 4.62 (doublet of pentets, $^3J_{HP} = 8.1$ Hz and $^3J_{HF} = 11.7$ Hz, 4H, OCH_2CF_3), 8.21 (multiplet, 2H, *m*-H), 8.73 (multiplet, 1H, *p*-H), 9.06 ppm (multiplet, 2H, *o*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 2.2 (d, $^3J_{CP} = 3.0$ Hz, $SiMe_3$), 65.4 (doublet of quartets, $^2J_{CP} = 4.6$ Hz and $^2J_{CF} = 38.3$ Hz, OCH_2CF_3), 120.7 (q, $^1J_{CF} = 319.7$ Hz, OTf), 122.2 (doublet of quartet, $^3J_{CP} = 7.6$ Hz and $^1J_{CF} = 277.7$ Hz, OCH_2CF_3), 128.8 (d, $^2J_{CP} = 6.9$ Hz, *o*-C), 144.5 (d, $^3J_{CP} = 3.8$ Hz, *m*-C), 150.4 (s, *p*-C). ^{19}F NMR ($CDCl_3$): −78.6 (s, OTf), −75.0 ppm (t, $^3J_{FH} = 8.5$ Hz, OCH_2CF_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): −1.4 ppm (d, $^2J_{SiP} = 24.8$ Hz).

Preparation of [4,4′-bipyridine·$P(OCH_2CF_3)_2{=}NSiMe_3$]OTf ([15b]OTf). A 1 mL solution of **12** (0.44 g, 1.11 mmol) in $CHCl_3$ was added dropwise to a suspension of 4,4′-bipyridine (0.17 g, 1.11 mmol) and AgOTf (0.28 g, 1.11 mmol) in 10 mL of $CHCl_3$ at 25 °C (in the absence of light). A white precipitate formed after stirring for 16 h. The white suspension was filtered and solvent removed in vacuo, yielding an off-white solid. Recrystallization from a 4:1 CH_2Cl_2/hexanes mixture afforded large colorless plates of **[15b]OTf** (0.28 g, 41%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −25.1 ppm (s). ^1H NMR ($CDCl_3$): 0.19 (s, 9H, $SiMe_3$), 4.59 (doublet of pentets, $^3J_{HP} = 8.1$ Hz and $^3J_{HF} = 11.7$ Hz, 4H, OCH_2CF_3), 7.68 (d, $J = 6.0$ Hz, 2H, *m*-H), 8.36 (d, $J = 5.1$ Hz, 2H, *m*-H), 8.76 (d, $J = 6.0$ Hz, 2H, *o*-H), 9.06 ppm (multiplet, 2H, *o*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 2.5 (d, $^3J_{CP} = 3.5$ Hz, $SiMe_3$), 65.8 (doublet of quartet, $^2J_{CP} = 4.6$ Hz and $^2J_{CF} = 38.5$ Hz, OCH_2CF_3), 121.2 (q, $^1J_{CF} = 320.4$ Hz, OTf), 122.6 (doublet of quartets, $^3J_{CP} = 8.6$ Hz and $^1J_{CF} = 277.8$ Hz, OCH_2CF_3), 126.8 (d, $^3J_{CP} = 7.2$ Hz, *m*-C), 128.8 (d, $^3J_{CP} = 6.7$ Hz, *m*-C′), 141.4 (s, *p*-C′), 145.2 (d, $^4J_{CP} = 4.4$ Hz, *p*-C), 148.8 (s, *o*-C′), 159.6 ppm (d, *o*-C). ^{19}F NMR ($CDCl_3$): −78.7 (s, OTf), −75.0 ppm (t, $^3J_{FH} = 8.5$ Hz, OCH_2CF_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): −5.3 ppm (s, $SiMe_3$). Anal. Calcd for $C_{18}H_{21}F_9N_3O_5PSSi$ (621.50): %C, 34.79; %H, 3.40; %N, 6.76. Found: %C, 33.28; %H, 3.37; %N, 6.60.

Preparation of [quinuclidine·$P(OCH_2CF_3)_2{=}NSiMe_3$]OTf ([15c]OTf). A 5 mL $CDCl_3$ solution of **12** (0.57 g, 1.44 mmol) was added to a stirring white suspension of quin (0.16 g, 1.44 mmol) and AgOTf (0.37 g, 1.44 mmol) in 10 mL of $CDCl_3$. After stirring for 2 days in the absence of light, the white suspension was filtered and the filtrate was evaporated to dryness, resulting in an off-white solid. Recrystallization from a 4:1 CH_2Cl_2/hexanes mixture yielded **[15c]OTf** as colorless needles (0.55 g, 66%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −15.0 ppm (s). ^1H NMR ($CDCl_3$): 0.22 (s, 9H, $SiMe_3$), 2.14 (br multiplet, 6H, NCH_2CH_2), 2.32 (d, 1H, CH), 3.70 (t, 6H, NCH_2CH_2), 4.60 ppm (doublet of pentets, $^3J_{HP} = 8.1$ Hz and $^3J_{HF} = 11.7$ Hz, 4H, OCH_2CF_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 2.4 (d, $^3J_{CP} = 3.1$ Hz, $SiMe_3$), 19.0 (s, CH), 23.2 (s, NCH_2CH_2), 55.6 (s, NCH_2CH_2), 65.6 (doublet of quartet, $^2J_{CP} = 6.0$ Hz and $^2J_{CF} = 38.9$ Hz, OCH_2CF_3), 120.9 (q, $^1J_{CF} = 319.8$ Hz, OTf), 122.1 ppm (doublet of quartets, $^3J_{CP} = 6.6$ Hz and $^1J_{CF} = 277.8$ Hz, OCH_2CF_3). ^{19}F NMR ($CDCl_3$): −78.6 (s, OTf), −75.0 ppm (t, $^3J_{FH} = 8.5$ Hz, OCH_2CF_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): −2.6 ppm (d, $^2J_{SiP} = 24.2$

(24) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *41*, 1690.
(25) Sheldrick, G. M. *SHELXTL−Windows NT. V6.12*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.

Scheme 2



7, 12

X = R = Cl (**7**)
X = Br; R = OCH_2CF_3 (**12**)

R = Cl (**[13]**$^+$)
R = OCH_2CF_3 (**[14]**$^+$)
X = OTf, Br, Cl

Hz, $SiMe_3$). Anal. Calcd for $C_{18}H_{21}F_9N_3O_5PSSi$ (621.50): %C, 31.25; %H, 4.54; %N, 4.86. Found: %C, 31.04; %H, 4.58; %N, 4.82.

Preparation of [quinuclidine·P(OCH$_2$CF$_3$)$_2$═NSiMe$_3$]Br ([15c]-Br). A 5 mL $CDCl_3$ solution of **12** (0.32 g, 0.82 mmol) was treated with a 2 mL $CDCl_3$ solution of quin (0.09 g, 0.82 mmol). The resulting clear colorless solution was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, and the quantitative conversion of **12** to **[15c]Br** was observed after 48 h. The reaction solution was reduced to dryness, which afforded a crystalline white solid (0.28 g, 69%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −14.6 ppm (s). ^1H NMR ($CDCl_3$): 0.18 (s, 9H, $SiMe_3$), 2.13 (br multiplet, 6H, NCH_2CH_2), 2.30 (d, 1H, CH), 3.68 (t, 6H, NCH_2CH_2), 4.57 ppm (doublet of pentets, $^3J_{HP}$ = 8.0 Hz and $^3J_{HF}$ = 11.8 Hz, 4H, OCH_2CF_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 2.4 (d, $^3J_{CP}$ = 3.1 Hz, $SiMe_3$), 19.0 (s, CH), 23.2 (s, NCH_2CH_2), 55.6 (s, NCH_2CH_2), 65.6 (doublet of quartets, $^2J_{CP}$ = 5.9 Hz and $^2J_{CF}$ = 38.8 Hz, OCH_2CF_3), 120.9 (q, $^1J_{CF}$ = 320.0 Hz, OTf), 122.1 ppm (doublet of quartet, $^3J_{CP}$ = 6.7 Hz and $^1J_{CF}$ = 277.8 Hz, OCH_2CF_3). ^{19}F NMR ($CDCl_3$): −78.6 (s, OTf), −75.0 ppm (t, $^3J_{FH}$ = 8.5 Hz, OCH_2CF_3).

Preparation of [quinuclidine·PCl$_2$═NSiMe$_3$]OTf ([16]OTf). To a stirring suspension of AgOTf (0.14 g, 0.53 mmol) and quin (0.06 g, 0.53 mmol) in 3 mL of $CHCl_3$ was added a 1 mL $CHCl_3$ solution of **7** (0.12 g, 0.53 mmol). The resulting white suspension was allowed to stir for 2 days, in the absence of light, and was then filtered. The clear colorless filtrate was reduced to dryness, and the resulting white solid was recrystallized from a 4:1 mixture of $CH_3CN/CHCl_3$ (0.12 g, 52%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −25.0 ppm (s). ^1H NMR ($CDCl_3$): 0.11 (d, $^4J_{HP}$ = 2.8 Hz, 9H, $SiMe_3$), 1.92 (br multiplet, 6H, NCH_2CH_2), 2.15 (br multiplet, 1H, CH), 3.84 ppm (br multiplet 6H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 1.7 (d, $^3J_{CP}$ = 5.5 Hz, $SiMe_3$), 19.3 (s, CH), 23.4 (s, NCH_2CH_2), 52.1 (s, NCH_2CH_2), 120.7 ppm (q, $^1J_{CF}$ = 320.5 Hz, OTf).

Preparation of TfO(CF$_3$CH$_2$O)$_2$P═NSiMe$_3$ [19]Cl. A 3 mL CD_2Cl_2 solution of **7** (0.19 g, 0.84 mmol) was treated with a 2 mL solution of quin (0.09 g, 0.84 mmol). The resulting clear colorless solution was stirred for 7 days at room temperature. The reaction solution was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, and no changes in the substrate/product ratios were observed after 7 days. All volatiles were removed from the reaction solution and resulted in a white crystalline solid, which was recrystallized via Et_2O vapor diffusion onto a saturated 4:1 CH_3CN/CH_2Cl_2 solution of **[19]Cl** (0.14 g, 37%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −16.5 ppm (s).

In Situ Preparation of 21. In the absence of light, a 2 mL $CDCl_3$ solution of **12** (0.56 g, 1.42 mmol) was added quickly to a 2 mL $CDCl_3$ suspension of AgOTf (0.36 g, 1.42 mmol). The resulting white suspension was stirred for 16 h and allowed to settle. The clear colorless supernatant was decanted, and spectroscopic analysis was obtained using a small portion while the remainder was stored at −30 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −29.0 ppm (s). ^1H NMR ($CDCl_3$): 0.18 (d, $^3J_{HP}$ = 1.2 Hz, 9H, $SiMe_3$), 4.40 ppm (doublet of pentets, $^3J_{HP}$ = 1.5 Hz and $^3J_{HF}$ = 8.1 Hz, 4H, OCH_2CF_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 2.1 (d, $^3J_{CP}$ = 5.4 Hz, $SiMe_3$), 64.0 (doublet of quartets, $^2J_{CP}$ = 6.3 Hz and $^2J_{CF}$ = 38.2 Hz, OCH_2CF_3), 122.2 (d of q, $^3J_{CP}$ = 10.3 Hz and $^1J_{CF}$ = 277.5 Hz, OTf), 122.4 ppm (d of q, $^3J_{CP}$ = 13.3 Hz and $^1J_{CF}$ = 277.5 Hz, OCH_2CF_3). ^{19}F NMR ($CDCl_3$): −74.7 (s, OTf), −74.6 ppm (t, J_{FH} = 7.6 Hz, OCH_2CF_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): −4.4 ppm (d, $^2J_{SiP}$ = 22.9 Hz, $SiMe_3$). Upon the removal of $CDCl_3$ in vacuo, **21** decomposes to a mixture containing 30% $[(CF_3CH_2O)_2P{=}N]_3$ (**22**) and 70% $[(CF_3CH_2O)_2P{=}N]_n$ (**23**). Data for decomposition products: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 17.2 (s, $[(CF_3CH_2O)_2P{=}N]_3$), −6.9 ppm (s, $[(CF_3CH_2O)_2P{=}N]_n$). Precipitation of a concentrated solution containing **22** and **23** into hexanes yielded a tacky clear colorless material adhered to the flask.

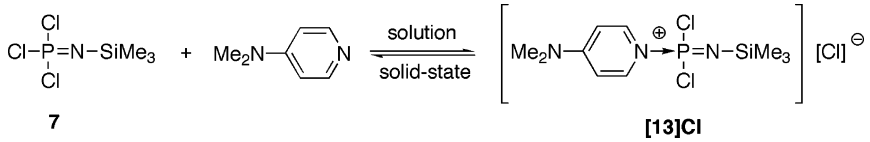
Preparation of [Br(CF$_3$CH$_2$O)$_2$P═NGaCl$_2$]$_2$ 24. To a 5 mL CH_2Cl_2 solution of **12** (0.48 g, 1.22 mmol) was added dropwise a 5 mL solution of $GaCl_3$ (0.21 g, 1.22 mmol) in CH_2Cl_2. After being stirred for 1 h, the resulting solution was reduced to dryness, yielding a colorless oil. Recrystallization from a 4:1 mixture of CH_2Cl_2/hexanes yielded clear colorless crystals identified by X-ray crystallography as $[Br(CF_3CH_2O)_2P{=}NGaCl_2]_2$ (0.83 g, 73%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 8.5 ppm (s). ^1H NMR ($CDCl_3$): 4.67 ppm (doublet of pentets, $^3J_{HP}$ = 7.8 Hz and $^3J_{HF}$ = 12.0 Hz, 4H, OCH_2CF_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 64.3 (d of q, $^2J_{CP}$ = 4.9 Hz and $^2J_{CF}$ = 38.1 Hz, OCH_2CF_3), 121.9 ppm (doublet of quartets, $^3J_{CP}$ = 8.3 Hz and $^1J_{CF}$ = 278.2 Hz, OCH_2CF_3). ^{19}F NMR ($CDCl_3$): −74.1 ppm (t, $^3J_{FH}$ = 8.5 Hz, OCH_2CF_3). EI-MS (70 eV, *m/z*, %): 891 (M^+−Cl, 45), 873 (M^+ − Cl − F, 71), and 829 (M^+ − OCH_2CF_3, 100). Anal. Calcd for $C_8H_8Br_2Cl_4F_{12}Ga_2N_2O_4P_2$ (927.15): %C, 10.36; %H, 0.87; %N, 3.02. Found: %C, 10.11; %H, 1.51; %N, 3.78.

Results and Discussion

In the reactions between **7** or **12** and DMAP in the presence of AgOTf, the quantitative formation of the DMAP-stabilized cations $[DMAP{\cdot}PCl_2{=}NSiMe_3]^+$ (**[13]**$^+$) and $[DMAP{\cdot}P(OCH_2CF_3)_2{=}NSiMe_3]^+$ (**[14]**$^+$), where OTf is the counteranion, was observed, and the salts **[13]OTf** and **[14]-OTf** were characterized in both solution and in the solid state (Scheme 2).[20,21] In the absence of AgOTf, the reactions between **7** or **12** and DMAP also quantitatively yielded the salts **[13]Cl** and **[14]Br**, respectively. However, only **[14]-Br** was found be stable in both solution and the solid state.[21] Thus, the salt **[13]Cl** slowly reconverts back to the parent phosphoranimine **7** and free DMAP (Scheme 3) in the solid state, yet reforms **[13]Cl** upon redissolving the material.[20]

Reactions of 7 and 12 with Pyridine or 4,4′-Bipyridine in the Presence or Absence of AgOTf. Since the employment of DMAP in the stabilization of phosphoranimine cations has proven to be successful in that the cations **[13]**$^+$ and **[14]**$^+$ could be generated even in the absence of the halide abstracting agent AgOTf, we decided to explore

Scheme 3



7 **[13]Cl**

Scheme 4

12
R = OCH_2CF_3

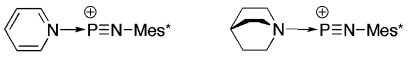
[15a]OTf, L = pyridine
[15b]OTf, L = 4,4′-bipyridine
[15c]OTf, L = quinuclidine

analogous chemistry involving **7** and **12** by employing the weaker nitrogen donors pyridine and 4,4′-bipyridine.

In the treatment of **7** with pyridine or 4,4′-bipyridine in CH_2Cl_2, no reaction was observed after 48 h. When the above reactions were repeated in the presence of AgOTf, the expected pyridine- or 4,4′-bipyridine-stabilized cations of **7** were not generated either. Instead, the formation of small quantities (<10%) of polydichlorophosphazene was observed after 48 h. Similarly, no reaction was observed between **12** and pyridine or 4,4′-bipyridine in CH_2Cl_2, yet treatment of **12** with pyridine or 4,4′-bipyridine in the presence of AgOTf resulted in the quantitative conversion of **12** ($^{31}P\{^1H\}$ NMR: −34 ppm) to new products with $^{31}P\{^1H\}$ NMR chemical shifts of −25 ppm (Scheme 4). The resultant products were isolated as white solids and comprehensively characterized as the new phosphoranimine salts **[15a]OTf** and **[15b]OTf** (Scheme 4). The solid-state structure of **[15b]OTf** was further confirmed from a single-crystal X-ray diffraction study (vide infra).

Reactions of 12 and 7 with quin in the Presence or Absence of AgOTf. The $^{31}P\{^1H\}$ NMR chemical shifts for the DMAP-, pyridine-, and 4,4′-bipyridine-stabilized cations of **12** all fall within a similar chemical shift range (**[14]**$^+$ = −22 ppm, **[15a]**$^+$ = −25 ppm, and **[15b]**$^+$ = −25 ppm). Therefore, we were interested to determine a relative chemical shift for the cation **[15]**$^+$ where a nonaromatic nitrogen base, such as quinucldine, is employed. Treatment of **12** with quin in the presence or absence of AgOTf quantitatively yielded the cation **[15c]**$^+$ and exhibited a $^{31}P\{^1H\}$ NMR chemical shift of −15 ppm. These salts **[15c]OTf** and **[15c]Br** were isolated and characterized by NMR spectroscopy, and a single-crystal X-ray diffraction study was carried out for **[15c]OTf** (Scheme 4).

As no reaction was observed between **7** and pyridine or 4,4′-bipyridine in the absence of AgOTf and the observation that small quantities of polydichlorophosphazene were generated in the presence of AgOTf, we concluded that both pyridine and 4,4′-bipyridine are bases that are too weak to stabilize the cation generated by abstraction of Cl^- from **7**. Therefore, we proceeded to perform analogous reactions involving the stronger, nonaromatic nitrogen-donor quin. When **7** was treated with quin in the presence of AgOTf, a new product with a $^{31}P\{^1H\}$ NMR chemical shift of −25 ppm was observed, and this product was characterized as the quin-stabilized phosphoranimine cation **[16]OTf** (Scheme 5). The $^{31}P\{^1H\}$ NMR chemical shift of −25 ppm for **[16]**$^+$ is significantly shifted downfield from the analogous DMAP-stabilized cation **[13]**$^+$ ($^{31}P\{^1H\}$ NMR: −40 ppm). Such a large downfield $^{31}P\{^1H\}$ NMR chemical shift upon altering the neutral donor from a pyridine-based ligand to quin has previously been noted. The $^{31}P\{^1H\}$ NMR chemical shift for the pyridine-bound cation **[17]**$^+$ is 71 ppm, whereas quin-bound cation **[18]**$^+$ exhibits a significantly downfielded $^{31}P\{^1H\}$ NMR chemical shift of 144 ppm.[26,27]



[17]$^+$ **[18]**$^+$
Mes* = 2,4,6-tri-tert-butylphenyl

In the absence of AgOTf, an unexpected result was observed. In a stoichiometric reaction between **7** and quin, the partial conversion (70%) of **7** ($^{31}P\{^1H\}$ NMR: −54 ppm) to two new products with $^{31}P\{^1H\}$ NMR chemical shifts of −16.5 (74%) and −16.1 ppm (26%) was observed. Upon workup, isolation, and purification, single crystals of the compound with a chemical shift of −16.5 ppm were obtained. From the single-crystal X−ray diffraction study, the major product that formed in the reaction between **7** and quin was the cationic amino-substituted phosphoranimine **[19]Cl**.[28] This product is believed to form via the quin-stabilized phosphoranimine salt **[16]Cl** whereby the coordination of quin to the cationic phosphorus center results in an electrophilic α-carbon which is prone to nucleophilic attack by an additional equivalent of quin in a mechanism similar to the Lewis acid-catalyzed polymerization of tetrahydrofuran (Scheme 5).[29]

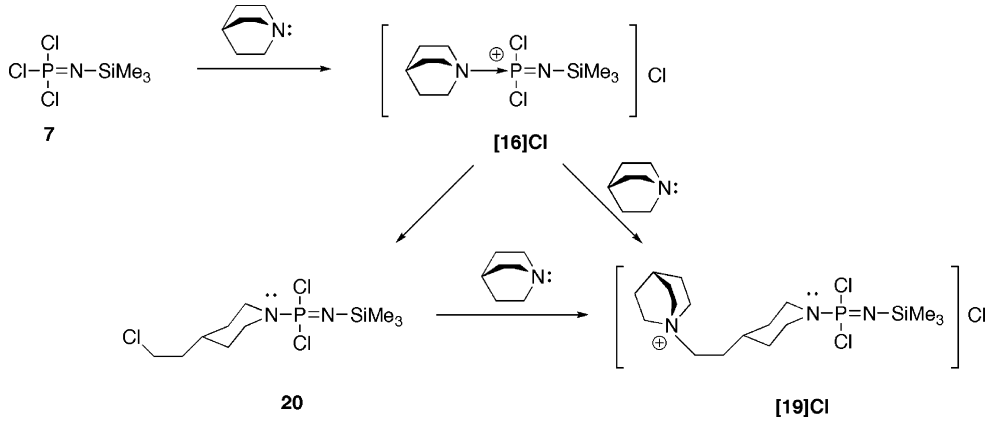
Alternatively, the nucleophile involved in the ring-opening reaction of **[16]**$^+$ may be the chloride counteranion where the resulting ring-opened product **20** would therefore be susceptible to a further nucleophilic substitution to yield the final product **[19]Cl**. Similar ring-opening reactions of quin involving halides,[30,31] aryl alcohols, amines, and imines as the nucleophile have been previously observed.[32] Thus, the product with a $^{31}P\{^1H\}$ NMR chemical shift of −16.1 ppm is tentatively assigned to the phosphoranimine intermediate **20**.

(26) Burford, N.; Losier, P.; Phillips, A. D.; Ragogna, P. J.; Cameron, T. S. *Inorg. Chem.* **2003**, *42*, 1087.
(27) Burford, N.; Cameron, T. S.; Robertson, K. N.; Phillips, A. D.; Jenkins, H. A. *Chem. Commun.* **2000**, 2087.
(28) A single-crystal X-ray diffraction study of **[19]Cl** revealed severely disordered $SiMe_3$ groups. Consequently, the structure could only be refined to an R ($I > 2\sigma(I)$) value of ca. 0.16. The study established the atom connectivity.
(29) Dreyfuss, P.; Dreyfuss, M. P. *Adv. Polym. Sci.* **1967**, *4*, 526.
(30) Pietra, F.; Biggi, G.; Del Cima, F. *J. Chem. Soc. C* **1971**, 3626.
(31) Reddy, N. D.; Elias, A. J.; Vij, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1515.
(32) Axelsson, O.; Peters, D. *J. Heterocyclic Chem.* **1997**, *34*, 461.

Table 1. Crystal Data for **[15b]OTf**, **[15c]OTf**, and **24**

	[15b]OTf	[15c]OTf	24
empirical formula	$C_{18}H_{21}F_9N_3O_5PSSi$	$C_{15}H_{26}F_9N_2O_5PSSi$	$C_8H_8Br_2Cl_4F_{12}Ga_2N_2O_4P_2$
fw	621.50	576.50	927.16
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	9.1226(12)	9.4473(3)	7.3377(4)
b (Å)	10.6662(13)	10.5320(6)	7.2197(4)
c (Å)	13.9961(13)	13.5145(7)	25.2792(12)
α (°)	87.268(8)	96.187(2)	90
β (°)	76.954(8)	110.049(3)	95.647(3)
γ (°)	88.781(5)	92.855(3)	90
V (Å^3)	1325.1(3)	1250.40(10)	1332.69(12)
Z	2	2	2
D_C (mg m^{-3})	1.558	1.531	2.311
temp (K)	150(1)	150(1)	150(1)
R ($I > 2\sigma(I)$)	0.0619	0.0587	0.0520
R_w ($I > 2\sigma(I)$)	0.1582	0.1684	0.1268
GOF on F^2	0.970	1.026	1.025

Scheme 5

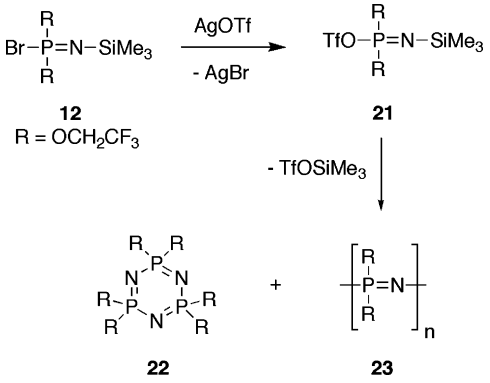


In an effort to test this postulate, **[16]OTf** was prepared in situ and was then treated with 1 equiv of $[Ph_4P]Cl$. Interestingly, instead of the formation of **20**, the complete retroconversion of **[16]OTf** to **7** was observed. This behavior has previously been noted for the DMAP-stabilized analogue **[13]Cl** (Scheme 3).[20,21] Moreover, addition of a further equivalent of quin to the above reaction mixture yielded the quantitative conversion of **7** to **[19]**$^+$ without observing the formation of **20**. While we do not rule out **20** as an intermediate, it is clearly likely that nucleophilic attack by quinuclidine on **[16]**$^+$ is the favored mechanism in the generation of **[19]**$^+$.

The formation of **[15c]Br**, **[15c]OTf**, and **[16]OTf** is quantitative, and these products do not undergo any further ring-opening reactions due to the poor basicity of the Br^- and OTf^- anions, compared to Cl^-. These observations thus further confirm the instability of nitrogen base-stabilized phosphoranimine cations bearing a chloride counteranion, which has been formerly noted for the salts **[13]Cl** and **[14]Cl**.[20,21]

Reactions of 7 and 12 with Other Halide-Abstraction Agents. We have previously reported the reaction between **7** and AgOTf in attempt to generate the triflato-substituted phosphoranimine $(TfO)Cl_2P{=}NSiMe_3$ (**18**).[20] The resultant product from this reaction was the quantitative formation of polydichlorophosphazene. Further attempts to prepare **18** by treatment of **7** with the electrophilic halide-abstracting agents Me_3SiOTf and MeOTf resulted in no reaction.

Scheme 6



In our present study, it is noted that the reactions between the phosphoranimine **12** and the aforementioned nitrogen bases yield the most stable cations such that **[14]**$^+$ and **[15]**$^+$ exhibit a clear enhancement in stability compared to **[13]**$^+$ and **[16]**$^+$, which were generated from the phosphoranimine **7**. Motivated by this observation, the phosphoranimine **12** was treated with AgOTf in $CDCl_3$ in an attempt to generate the triflato-substituted phosphoranimine **21** (Scheme 6). Analysis of the reaction mixture by NMR spectroscopy after 16 h revealed the quantitative conversion of **12** ($^{31}P\{^1H\}$ NMR: −34 ppm) to **21** ($^{31}P\{^1H\}$ NMR: −29 ppm).

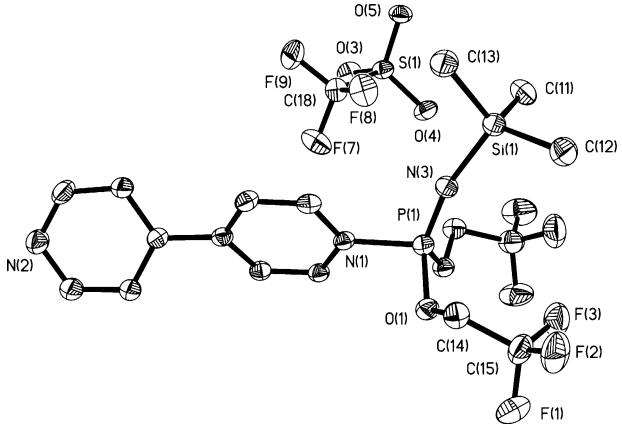


Figure 1. Thermal ellipsoid plot of **[15b]OTf** at the 50% probability level. All hydrogen atoms are omitted for clarity.

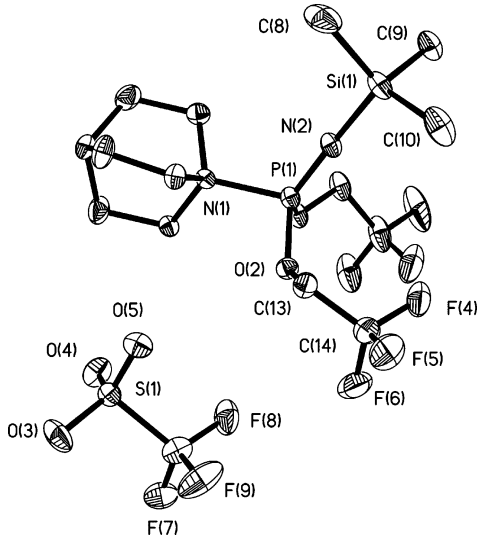


Figure 2. Thermal ellipsoid plot of **[15c]OTf** at the 50% probability level. All hydrogen atoms are omitted for clarity.

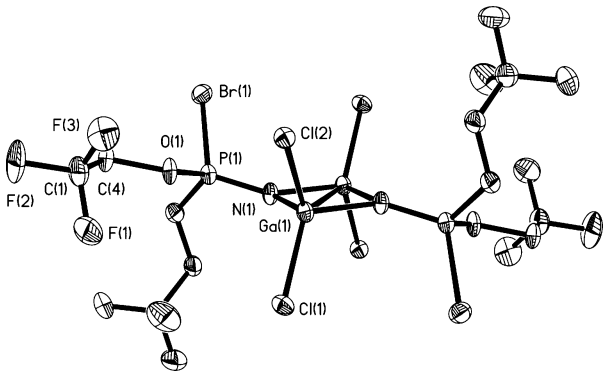
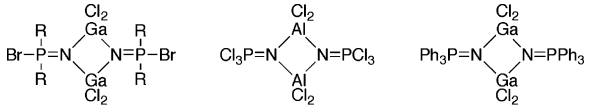


Figure 3. Thermal ellipsoid plot of **24** at the 50% probability level. All hydrogen atoms are omitted for clarity.

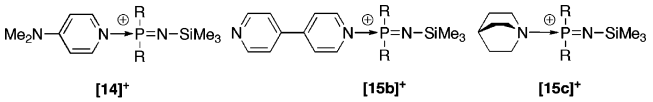
However, upon workup and the removal of solvent in vacuo, **21** decomposes to yield the cyclic phosphazene **22** ($^{31}P\{^1H\}$ NMR: 17 ppm)[33] and polybis(trifluoroethoxy)phosphazene **23** ($^{31}P\{^1H\}$ NMR: −7 ppm).[12] Attempts to isolate **23** and determine its molecular weight were unsuccessful. The addition of a concentrated CH_2Cl_2 solution containing **22** and **23** to rapidly stirring hexanes yielded a clear colorless material that adhered to the sides of the precipitation flask, a likely consequence of these materials possessing low molecular weight.

Encouraged by the successful application of the CF_3CH_2O substituent in these cationic systems, **12** was reacted with a stoichiometric amount of $GaCl_3$ with the goal of producing the base-free phosphoranimine salt $[(CF_3CH_2O)_2P{=}NSiMe_3][GaCl_3Br]$. This species would complement the family of methylenephosphonium cations that contain a trigonal planar phosphorus(V) center.[34] Analysis of the reaction mixture revealed a clean downfield shift from the phosphoranimine **12** to a new product with a $^{31}P\{^1H\}$ NMR shift of 8.5 ppm. This compound was isolated and characterized as the *N*-dichlorogallaphosphoranimine dimer **24**. Instead of halide abstraction from **12**, the formation of **24** in all likelihood resulted from the initial coordination of $GaCl_3$ to the nitrogen center of **12** followed by elimination of Me_3SiCl and dimerization. Similar results have been previously reported in the reaction between **7** and $AlCl_3$ (**25**),[35] as well as that between $Ph_3P{=}NSiMe_3$ and $GaCl_3$ (**26**).[36]



Structural Characterization of New Compounds by X-ray Diffraction. Views of the formula units for **[15b]OTf**, **[15c]OTf**, and **24** determined by X-ray crystallography (Table 1) are shown in Figures 1−3, and selected bond lengths and angles are given in Table 2. The phosphoranimine, P(1)−N(3), bond lengths observed for $[\mathbf{15b}]^+$ and $[\mathbf{15c}]^+$ are 1.484(3) and 1.481(3) Å, respectively, and are comparable to the P(1)−N(3) bond distance of 1.4894(18) Å found in the DMAP-stabilized derivative $[\mathbf{14}]^+$.[21] These phosphorus−nitrogen bond lengths are extremely short, where typical phosphorus−nitrogen double bonds range from 1.54 to 1.58 Å[37] and approach the observed the 1.475(8) Å bond length found in the iminophosphonium cation $[\mathbf{1}]^+$, where a formal triple bond exists between phosphorus(III) and nitrogen.[3]

The internal phosphoranimine nitrogen bond angles, P−N−Si, found in the cations $[\mathbf{15b}]^+$ and $[\mathbf{15c}]^+$ are 163.5-



(33) Schmutz, J. L.; Allcock, H. R. *Inorg. Chem.* **1975**, *14*, 2433.
(34) Guerret, O.; Bertrand, G. *Acc. Chem. Res.* **1997**, *30*, 486.
(35) Jäschke, B.; Jansen, M. *Z. Naturforsch. B: Chem. Sci.* **2002**, *57*, 1237.
(36) Heshmatpour, F.; Nusshär, D.; Garbe, R.; Wocadlo, S.; Massa, W.; Dehnicke, K.; Goesmann, H.; Fenske, D. *Z. Anorg. Allg. Chem.* **1995**, *621*, 443.
(37) Typical P=N bond lengths range from 1.54 to 1.58 Å: Allen, C. W. *Coord. Chem. Rev.* **1994**, *130*, 137.

Table 2. Selected Bond Lengths and Angles for **[15b]OTf**, **[15c]OTf**, **22**, and Related Compounds

	P−N(donor) [Å]	P═N [Å]	P−N−E [deg]	ref
[15b]$^+$	1.777(3)	1.484(3)	163.5(2) (E = Si)	this work
[15c]$^+$	1.800(3)	1.481(3)	174.16(19) (E = Si)	this work
[14]$^+$	1.7278(18)	1.4894(18)	159.63(15) (E = Si)	21
[17]$^+$	1.958(8)	1.472(8)	161.7(7) (E = C)	27
[18]$^+$	1.933(2)	1.519(2)	143.9(2) (E = C)	27
24	N/A	1.536(5)	127.0(3) (E = Ga)	this work
25	N/A	1.531(3)	134.5(2) (E = Al)	35
26	N/A	1.62(1)	134.2(5) (E = Ga)	36

(2)° and 174.16(19)°, respectively, and are considerably wider than the same bond angle of 159.63(15)° found in **[14]**$^+$. In particular, the bond angle of 174.16(19)° found in **[15c]**$^+$ approaches the P−N−C angle of 177.0(7)° found in **[1]**$^+$, where a formal sp-hybridized nitrogen center is present.[3]

While the internal phosphoranimine bond distances found in **[15b]**$^+$, **[15c]**$^+$, and **[14]**$^+$ are similar in length, the donor nitrogen−phosphorus bond distances for these cations vary significantly. The N(1)−P(1) bond length for **[14]**$^+$ is short at 1.7278(18) Å, yet the N(1)−P(1) bond lengths observed for **[15b]**$^+$ and **[15c]**$^+$ are noticeably longer at 1.777(3) and 1.800(3) Å, respectively, and approach the idealized phosphorus−nitrogen single bond length of 1.800(4) Å.[38] However, these bond lengths are significantly shorter than those of the analogous pyridine- and quin-stabilized iminophosphonium cations **[17]**$^+$ and **[18]**$^+$ of 1.958(8) and 1.933(2) Å, respectively.[27]

The short internal phosphoranimine P−N bond lengths and large P−N−Si bond angles found in the cations **[15b]**$^+$ and **[15c]**$^+$ suggest significant P−N multiple bond character. However, when using the traditional valence-bond model in describing the unsaturated phosphorus(V)−nitrogen bond, hypervalency at the phosphorus center and thus, d-orbital participation must be invoked for $d\pi_P-p\pi_N$ overlap to occur and form the formal π bond.[39,40] Recently, ab initio investigations have shown that d orbitals play an insignificant role in bonding involving the main-group elements[41,42] due to their high energy, and thus, an ionic bonding model is more suitable in describing the P(V)−N double bond in phosphoranimines.[43,44] While this bonding model accounts for the short phosphorus−nitrogen bond lengths found in the cations **[15b]**$^+$ and **[15c]**$^+$, it does not account for the observed wide nitrogen bond angles. To account for this structural feature, the negative hyperconjugation[45,46] model must be employed. In this model, the short P−N bond lengths can be rationalized from the interaction of the nitrogen lone pair π_N orbital with the highly polarized σ^*_{PR} orbitals.[47] However, by employment of the extremely electronegative CF_3CH_2O substituent, the energy of the σ^*_{PR} orbitals is lowered and thus permits more efficient $\pi_N-\sigma^*_{PR}$ overlap and hence results in the extremely wide nitrogen bond angles observed in **[15b]**$^+$ and **[15c]**$^+$.

The phosphoranimine cations **[15a−c]**$^+$ represent nitrogen donor-stabilized surrogates of the proposed intermediate (**[9]**$^+$) in the thermal condensation polymerization of phosphoranimimines. While these salts do not initiate or undergo polymerization, they serve as excellent model complexes that aid in the understanding of structure and reactivity of **[9]**$^+$. Ongoing investigations in the preparation and reactivity of phosphoranimine cations bearing phosphorus donors are underway in an attempt to better understand the thermal condensation polymerization mechanism of phosphoranimines.[48,49] Moreover, the cations **[15b,c]**$^+$ exhibit unconventional bonding features which challenge traditional bonding models involving the P(V)−N multiple bond and offers new structural insights into this long-established bonding motif.

Conclusions

A series of pyridine and aliphatic amine based donor-stabilized phosphoranimine cations have been prepared and structurally characterized. The cations represent models of the proposed intermediate in the thermal condensation polymerization of phosphoranimines. The preparation of these cations requires the use of strong bases, such as DMAP or quin, with or without the halide-abstraction reagent AgOTf, and the stability of the corresponding salts were found to be highly counteranion dependent. In contrast to DMAP, employment of weaker nitrogen bases such as pyridine or 4,4′-bipyridine do not yield stable cations in the absence of highly electron-withdrawing substituents on the phosphoranimine. In addition, the use of the halide-abstraction reagent AgOTf is necessary for cation formation. These observations give further insight into the highly reactive nature of donor-stabilized cationic phosphoranimines and the necessity of having strong donors coupled with weakly coordinating counteranions to allow base-stabilized species to be generated and to be stable and isolable. Structural studies of the cations reveal short internal phosphorus(V)−nitrogen bond lengths and wide nitrogen bond angles, which suggest multiple P−N bond character, yet are rationalized by a currently underutilized negative hyperconjugation bonding model.

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(38) Cameron, T. S.; Chan, C.; Chute, W. J. *Acta Crystallogr.* **1980**, *B36*, 2391.
(39) Dewar, M. J. S.; Lucken, E. A. C.; Whitehead, M. A. *J. Chem. Soc.* **1960**, 2423.
(40) Mitchell, K. A. R. *Chem. Rev.* **1969**, *69*, 157.
(41) Magnusson, E. *J. Am. Chem. Soc.* **1993**, *115*, 1051.
(42) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339.
(43) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Butterworth Heinemann: New York, 2002.
(44) Kocher, N.; Leusser, D.; Murso, A.; Stalke, D. *Chem. Eur. J.* **2004**, *10*, 3622.
(45) Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3969.
(46) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.
(47) Chaplin, A. B.; Harrison, J. A.; Dyson, P. J. *Inorg. Chem.* **2005**, *44*, 8407.
(48) Huynh, K.; Rivard, E.; LeBlanc, W.; Blackstone, V.; Lough, A. J.; Manners, I. *Inorg. Chem.* **2006**, *45*, 7922.
(49) Huynh, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2006**, *128*, 14002.

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Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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