Donor-Stabilized Cations and Imine Transfer from *N*-Silylphosphoranimines

Eric Rivard, Keith Huynh, Alan J. Lough, and Ian Manners*

*University of Toronto, Department of Chemistry, Davenport Laboratories, 80 St. George Street,
Toronto, Ontario, Canada M5S 3H6*

Received November 11, 2003; E-mail: imanners@chem.utoronto.ca

N-Silylphosphoranimines $R_3P{=}NSiR'_3$ are of considerable interest as model species with phosphorus–nitrogen multiple bonds[1] and as polymer precursors.[2] Cationic *N*-silylphosphoranimines $[R_2P{=}NSiR'_3]^+$ are currently unknown but have been considered[3] as possible intermediates in the formation of polyphosphazenes[4] via thermally induced condensation polymerization and would be expected to exhibit interesting reactivity. In this communication we report on our attempts to prepare the cation $[Cl_2P{=}NSiMe_3]^+$ and the discovery of an unusual imine transfer reaction involving phosphorus centers.

Initial attempts to generate an *N*-silylphosphoranimine cation involved the reaction of $Cl_3P{=}NSiMe_3$ (**1**)[5] with the halide abstractor Ag[OTf] (OTf = OSO_2CF_3) in CH_2Cl_2. In lieu of obtaining the triflato derivative $(TfO)PCl_2{=}NSiMe_3$ (**2**), the quantitative formation of poly(dichlorophosphazene) $[Cl_2P{=}N]_n$ and $TfOSiMe_3$ was detected by ^1H, ^{19}F, and ^{31}P NMR spectroscopy. Attempts to trap **2** by performing the reaction in arene solvents (C_6D_6 and toluene)[6] or at low temperature ($-70\ °C$) gave similar results. Use of substoichiometric quantities (10–20 mol %) of Ag[OTf] led to the incomplete consumption of **1** (ca. 70%) over a period of 2 weeks to yield $[Cl_2P{=}N]_n$ and cyclic phosphazene oligomers $[Cl_2P{=}N]_x$, $x = 3{-}5$. These results suggest that if **2** is indeed generated initially, it rapidly oligomerizes due to the labile OTf group at phosphorus.

Encouraged by the successful application of coordinating pyridine derivatives to stabilize cationic phosphorus(III)[7] and, in some cases, phosphorus(V) centers,[7c,d,8] we repeated the reaction of **1** and Ag[OTf] in the presence of the strong donor 4-(dimethylamino)-pyridine (DMAP). Upon combining these reagents in CH_2Cl_2 the immediate formation of a white precipitate (AgCl) was observed. Analysis of the reaction mixture by ^{31}P NMR spectroscopy indicated that the clean conversion of **1** ($\delta = -54$ ppm) had occurred to yield a new product with a downfield-shifted resonance at -40 ppm. This species was isolated as colorless needles (mp = 98–100 °C) and identified as the novel cationic phosphoranimine salt, $[DMAP{\cdot}PCl_2{=}NSiMe_3]OTf$, **[3]OTf** by X-ray diffraction (Figure 1). Despite the existence of numerous (>500) different phosphoranimine derivatives, **[3]OTf** represents, to our knowledge, the first crystallographically characterized cationic member of this family.[9]

The X-ray study of **[3]OTf**[10] revealed that a very short internal phosphazene $[P(1){-}N(3)]$ bond length of 1.490(3) Å was present,[11] which approaches those observed within the triply bonded iminophosphenium cations $RN{\equiv}P^+$ (1.46–1.49 Å);[12] consequently, a wide P–N–Si bond angle of 144.1(2)° is observed. The DMAP ligand is strongly bound to the phosphorus center in **[3]OTf** and lies at a distance of 1.713(2) Å $[P(1){-}N(1)]$. As a point of reference, the $P{-}N_{DMAP}$ distances within the bis(imino)phosphonium adduct $[(DMAP)_2P({=}NMes^*)_2]^+$ (**4**) (Mes* = 2,4,6-$^tBu_3C_6H_2$)[8a] are quite elongated [1.812(4) and 1.830(4) Å]. These data suggest that the $[Cl_2P{=}NSiMe_3]^+$ cation, if isolated in free form, would be highly electrophilic. The OTf^- counterion in **[3]OTf** exists as a spectator
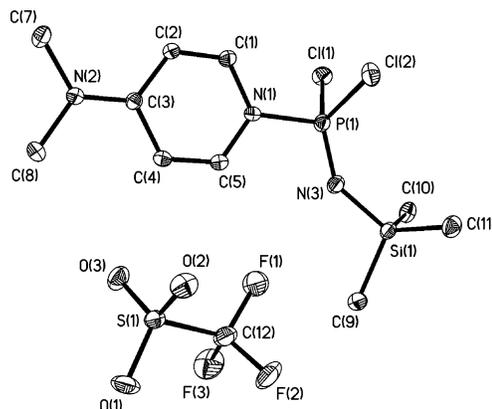

Figure 1. Molecular structure of **[3]OTf** with thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity.

with the closest anion–cation contact [4.0 Å: $N(3){-}F(1)$] still well outside the sum of the van der Waals radii for the constituent atoms.

From the structural data presented, two plausible resonance contributors, **I** and **II**, help describe the bonding within **[3]⁺**:
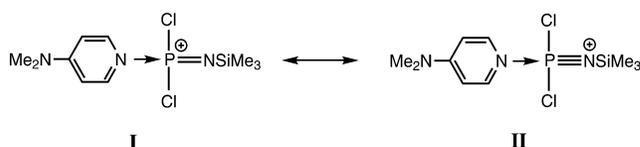
Interestingly, the reaction of DMAP with **1** also gave **[3]⁺** in the absence of a halide abstractor; however, the reaction times were appreciably longer (2 h vs 5 min). Remarkably, the product, **[3]Cl**, slowly reconverts into **1** and DMAP in the solid state, with 95% conversion after 14 d at 20 °C. This process is reversible as dissolution of the products in CH_2Cl_2 regenerated **[3]Cl** after a few hours. The equilibrium between **[3]Cl** and the precursors **1** and free DMAP was further confirmed by the addition of $[Ph_3P{=}N{=}PPh_3]Cl$, which led to complete retroconversion of **[3]Cl** after 1.0 equiv of Cl^- was added. It is likely that the recombination of **[3]⁺** and Cl^- in the solid state is promoted by their close proximity in this phase.

The analogous salts **[3]BF₄** and **[3]SbF₆** were prepared from DMAP, **1**, and either $Ag[BF_4]$ or $Ag[SbF_6]$ in CH_2Cl_2. While the hexafluoroantimonate salt **[3]SbF₆** proved indefinitely stable in solution, **[3]BF₄** slowly decomposed within 3 days to give a mixture of $DMAP{\cdot}BF_3$, the cyclic phosphazene $[Cl_2P{=}N]_3$, and presumably volatile $FSiMe_3$ (Scheme 1). One possible route which explains the formation of phosphazene oligomers involves the initial formation of (undetected) $FCl_2P{=}NSiMe_3$ (**5**) via the addition of a BF_4^--derived fluoride ion to **[3]⁺**, followed by the combination of the BF_3 and DMAP byproducts to give $DMAP{\cdot}BF_3$. Condensation of **5** with the elimination of $FSiMe_3$ could then produce $[Cl_2P{=}N]_3$. Repeated attempts to generate **5** independently from **1** and

Scheme 1
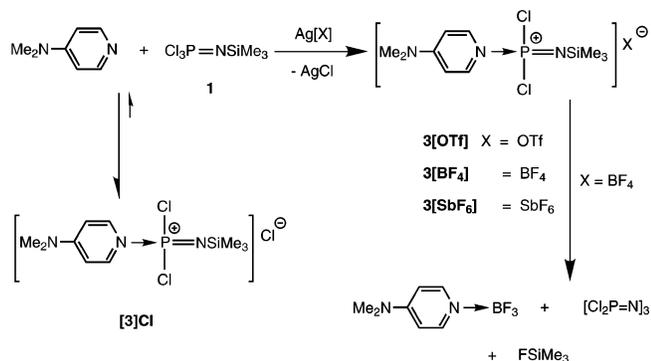
various fluorinating agents (e.g., Ag[BF$_4$]) gave highly complicated reaction mixtures consistent with the formation of partially fluorinated phosphazene oligomers [F$_{2-y}$Cl$_y$P=N]$_x$. The increased stability of [3]SbF$_6$ supports the delivery of fluoride to [3]$^+$ as the initial step in the decomposition of [3]BF$_4$. The SbF$_6^-$ ion is particularly resistant to fluoride ion transfer, and consequently, is often employed to facilitate the isolation of highly reactive cations (e.g., S$_4^{2+}$).[13]

The successful isolation of the amine donor-stabilized phosphoranimine cation [3]$^+$ prompted us to attempt the synthesis of an analogous phosphine-stabilized cation [R$_3$P·PCl$_2$=NSiMe$_3$]$^+$ (6). Such a species would complement the burgeoning area of P(III) → P(III) coordination chemistry.[14] Surprisingly, when 1 was allowed to combine with phosphines PR$_3$ (R = Ph and ^{n}Bu) in CH$_2$Cl$_2$ (25 °C, 24 h and 6 d), the known N-phosphinophosphoranimines R$_3$P=N−PCl$_2$ (R = Ph and ^{n}Bu; 7 and 8) were formed along with a stoichiometric quantity of ClSiMe$_3$. Monitoring the reaction by ^{1}H and ^{31}P NMR spectroscopy revealed the initial formation of PCl$_3$ and R$_3$P=NSiMe$_3$ prior to the formation of 7 and 8 (Scheme 2). This observation is striking as the initial step in the reaction can be formally regarded as an example of an imine-transfer reaction involving two phosphorus centers.

Scheme 2
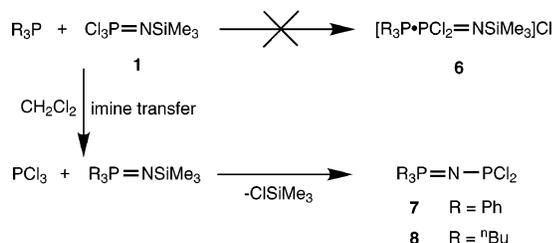
This process may indeed involve the formation of a phosphine-stabilized cation 6, followed by imine transfer to R$_3$P via a three-membered intermediate or transition state (with PCl$_3$ as a byproduct). However, we have yet to be able to detect 6, and the direct attack of the phosphine at nitrogen also needs to be considered. Although the delivery of imine functionality to phosphines is well-known using organoazide reagents (Staudinger reaction),[15] other examples of such a transformation still remain very rare.[16,17]

In summary, the successful synthesis of a novel donor-stabilized N-silylphosphoranimine cation has been reported, whose stability is intimately linked with the nature of the counterion. Attempts to prepare a phosphine-donor analogue uncovered an unusual imine transfer reaction. Studies directed at elucidating the mechanism and scope of the imine transfer reaction, and the isolation of the hitherto unknown cation [R$_3$P·PCl$_2$=NSiR′$_3$]$^+$ are in progress.

Supporting Information Available: Experimental details for the synthesis and characterization of new compounds (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993. p 403.

(2) (a) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848. (b) Montague, R. A.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1990**, *112*, 6721. (c) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035.

(3) (a) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541. (b) Cationic P(V)−N intermediates have also been implicated in the formation of polyphosphazenes by ring-opening polymerization of [Cl$_2$P=N]$_3$: Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315.

(4) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, New Jersey, 1992.

(5) (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.

(6) It was hoped that electrophilic attack of 2 on the arene would yield arylated species ArPCl$_2$=NSiMe$_3$.

(7) (a) Burford, N.; Losier, P.; Phillips, A. D.; Ragogna, P. J.; Cameron, T. S. *Inorg. Chem.* **2003**, *42*, 1087. (b) Weiss, R.; Engel, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 216. (c) Weiss, R.; Engel, S. *Synthesis* **1991**, 1077. (d) Bouhadir, G.; Reed, R. W.; Réau, R.; Bertrand, G. *Heteroatom. Chem.* **1995**, *6*, 371.

(8) (a) Blättner, M.; Nieger, M.; Ruban, A.; Schoeller, W. W.; Niecke, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2768. (b) Nilsson, J.; Kraszewski, A.; Stawinski, J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2263.

(9) Our definition excludes species that are protonated at nitrogen, e.g., R$_3$P=NHR$^+$. Examples of [R$_2$P=NR′]$^+$ cations have been reported; however, none were characterized by X-ray crystallography: (a) Mulliez, M.; Majoral, J.-P.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1984**, 284. (b) Marre-Mazières, M. R.; Sanchez, M.; Wolf, R.; Bellan, J. *New J. Chem.* **1985**, *9*, 605. (c) Becker, W.; Jones, P. G.; Schomburg, D.; Schmutzler, R. *Chem. Ber.* **1990**, *123*, 1759.

(10) See Supporting Information for full crystallographic details.

(11) For comparison, typical P=N phosphazene bond lengths range from 1.54 to 1.58 Å: Allen, C. W. *Coord. Chem. Rev.* **1994**, *130*, 137.

(12) (a) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715. (b) 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.

(13) Murchie, M. P.; Passmore, J.; Sutherland, G. W.; Kapoor, R. *J. Chem. Soc., Dalton Trans.* **1992**, 503.

(14) (a) Spangenberg, S. F.; Sisler, H. H. *Inorg. Chem.* **1969**, *8*, 1006. (b) Burford, N.; Ragogna, P. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4307. (c) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 14404.

(15) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353.

(16) (a) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186 and references therein. (b) Fluck, v. E.; Hösle, R. *Z. Anorg. Allg. Chem.* **1979**, *458*, 103. (c) Fluck, v. E.; Hösle, R.; Zischka, A.-K. *Z. Anorg. Allg. Chem.* **1981**, *474*, 105. (d) For the use of phosphoranimines as imine metathesis catalysts see: Bell, S. A.; Meyer, T. Y.; Geib, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 10698.

(17) Metathesis reactions have also been reported involving P=P bonds and phosphines PR$_3$: see (a) Smith, R. C.; Shah, S.; Urnezius, E.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2003**, *125*, 40. (b) Kovacs, I.; Matern, E.; Sattler, E.; Fritz, G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1819. (c) Cowley, A. H.; Cushner, M. C. *Inorg. Chem.* **1980**, *19*, 515.

JA039549Z