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Reactions of P-Donor Ligands with *N*-Silyl(halogeno)organophosphoranimines: Formation of Cations with P−P Coordination Bonds and Poly(alkyl/aryl)phosphazenes at Ambient Temperature

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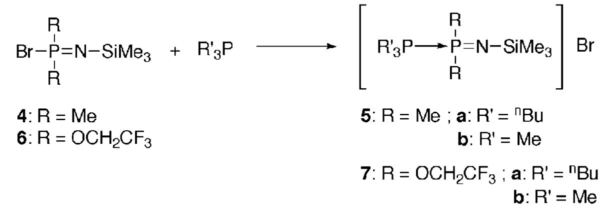
N-Silylphosphoranimines have played an important role in the development of molecular main group,[1] coordination,[2] and inorganic polymer chemistry as precursors to polyphosphazenes.[3−5] Cationic *N*-silylphosphoranimines $[R_2P{=}NR']^+$ are believed to be involved in the thermal condensation polymerization route to poly(alkyl/aryl)phosphazenes[3c] from organophosphoranimines at 150−190 °C, and related cyclic P(V)−N cations have been implicated as intermediates in the formation of polyphosphazenes by thermal ring-opening polymerization of $[Cl_2P{=}N]_3$ at 250 °C.[6] However, despite their potentially interesting reactivity, very few studies of these cationic species have been reported.[7]

In 2004, we reported the preparation of the cationic phosphoranimine salt $[DMAP{\cdot}PCl_2{=}NSiMe_3]Cl$ (**2**),[8] which is stabilized by the strong N-donor 4-(dimethylamino)pyridine (DMAP), from the direct reaction between $Cl_3P{=}NSiMe_3$ (**1**)[9] and DMAP. In an effort to diversify this chemistry to the formation of phosphoranimine cations stabilized by P-donor ligands, we have also studied the reactions of **1** and tertiary phosphines. Significantly, if successful, this would provide a route to species which would complement the recently prepared series of P(III)→P(III) adducts, known as phosphine−phosphenium cations.[10] However, we found that reactions between **1** and R_3P ($R = {}^n$Bu or Ph) yielded the known *N*-phosphinophosphoranimines $R_3P{=}N{-}PCl_2$ (**3**) via a complex mechanism which involves a series of dechlorination and condensation steps.[11] These results indicated that the presence of a trichloro functionality at phosphorus in the phosphoranimine was incompatible with the preparation of the desired P(III)→P(V) cations by this route. In this communication, we report on our preliminary studies of the reactions of *mono*halogenoorganophosphoranimines $XR_2P{=}NSiMe_3$ with P-donor ligands. This has led to the first examples of P-donor-stabilized phosphoranimine cations and also a new route to poly(alkyl/aryl)phosphazenes at room temperature.

$^{31}P\{^1H\}$ NMR analysis showed that treatment of a $CHCl_3$ solution of the phosphoranimine $BrMe_2P{=}NSiMe_3$ (**4**) [$\delta(^{31}P) = 10$ ppm][12] with $^n Bu_3P$ [$\delta(^{31}P) = -30$ ppm] resulted in the quantitative conversion to a new product with two doublets [$\delta(^{31}P) = -1$ and 8 ppm, $^1J_{PP} = 23$ Hz]. This product was characterized as the novel phosphine-stabilized cationic phosphoranimine salt $[^n Bu_3P{\cdot}PMe_2{=}NSiMe_3]Br$ (**[5a]Br**) by multinuclear NMR (Scheme 1).[13] While the ^{31}P NMR shifts for this cation are expected for such a species, the $^1J_{PP}$ observed is unusually small in comparison with other P−P bonded compounds.[14]

To explore the generality of this chemistry, the phosphoranimine **4** was treated with the less basic phosphine Ph_3P. However, in this case, no reaction was detected by $^{31}P\{^1H\}$ NMR. As expected, the basic phosphine Me_3P was found to react in a manner similar to $^n Bu_3P$ (Scheme 1). In this case, addition of a 1 M toluene solution of Me_3P [$\delta(^{31}P) = -60$ ppm] to **4** in $CHCl_3$ led to the immediate precipitation of a white solid. The $^{31}P\{^1H\}$ NMR spectrum of the suspension was recorded after 18 h and revealed the formation of the cationic phosphoranimine salt $[Me_3P{\cdot}PMe_2{=}NSiMe_3]Br$ (**[5b]Br**) as two doublets centered at −1 and 3 ppm with a $^1J_{PP}$ of 13 Hz. After workup and recrystallization, the molecular structure of **[5b]Br** was confirmed by a single-crystal X-ray diffraction study.[13]

Scheme 1



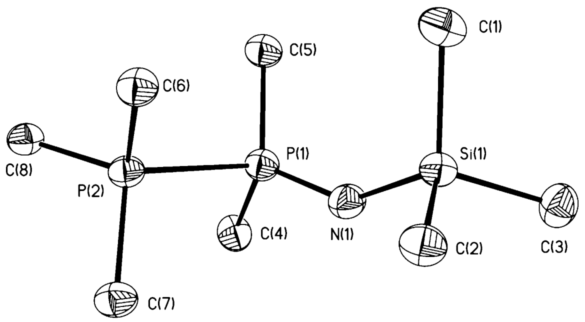


Figure 1. Molecular structure of the cation in **[5b]Br** with thermal ellipsoids at the 30% probability level. All hydrogen atoms and the bromide counteranion are omitted for clarity.

The solid-state structure of **[5b]Br** (Figure 1) revealed a P(1)−P(2) bond length of 2.2229(11) Å which is slightly elongated from typical sterically unencumbered phosphorus−phosphorus single bond lengths (2.20 Å).[15] The P(1)−N(1) bond length of 1.533(3) Å and the P(1)−N(1)-Si(1) angle of 143.98(16)° is in agreement with characteristic phosphoranimine bond lengths and angles.[16]

We also explored the potential expansion of this chemistry to the phosphoranimine $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**6**),[12] which bears electron-withdrawing trifluoroethoxy substituents (Scheme 1). When a solution of $^n Bu_3P$ was added rapidly to a $CHCl_3$ solution of **6** [$\delta(^{31}P) = -35$ ppm], $^{31}P\{^1H\}$ NMR showed clean conversion to a single new product which exhibited two doublets at −18 and 22 ppm and a $^1J_{PP}$ of 277 Hz. This product was characterized as the phosphine-stabilized phosphoranimine salt $[^n Bu_3P{\cdot}P(CF_3CH_2O)_2{=}NSiMe_3]Br$ (**[7a]Br**).[13] Similarly, the phosphoranimine **6** was treated with a 1 M toluene solution of Me_3P. After stirring for 18 h, the

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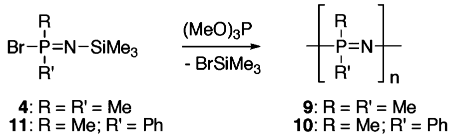
reaction solution was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy and revealed the quantitative conversion of **6** and Me_3P to the Me_3P-stabilized phosphoranimine salt $[Me_3P{\cdot}P(CF_3CH_2O)_2{=}NSiMe_3]Br$ (**[7b]Br**), which exhibits two doublets centered at −16 and 12 ppm with a $^1J_{PP}$ of 324 Hz.

Significantly, the values of the $^1J_{PP}$ coupling constants were much larger in the cases of **[7a]**$^+$ and **[7b]**$^+$ (277 and 324 Hz, respectively) compared to those for **[5a]**$^+$ and **[5b]**$^+$ (23 and 13 Hz). The smallest $^1J_{PP}$ values are observed when electron-donating Me substituents rather than electron-withdrawing substituents are present in the phosphoranimine moiety. These observations suggest that an electron push−pull mechanism is present which significantly influences the magnitude of the $^1J_{PP}$ in these systems.

In an attempt to extend this new chemistry to phosphoranimine cations with phosphites instead of phosphines as the stabilizing P-donor ligand, we treated the phosphoranimine $BrMe_2P{=}NSiMe_3$ (**4**) with $(MeO)_3P$ in $CHCl_3$. In this case, $^{31}P\{^1H\}$ NMR analysis of the products after 4 h showed that the salt $[(MeO)_3P{\cdot}PMe_2{=}NSiMe_3]Br$ (**8**) was not formed. Instead, quantitative conversion of **4** to the known polyphosphazene $[Me_2P{=}N]_n$ (**9**) [$\delta(^{31}P) = 7$ ppm][3a] was detected (Scheme 2). The polymer **9** was isolated in high yield as a white fibrous solid by precipitation into pentane and was shown to be of high molecular weight by dynamic light scattering measurements.[13]

Scheme 2



To explore the potential generality of this new route, we attempted to prepare polyphosphazene $[MePhP{=}N]_n$ (**10**) via an analogous method. Treatment of the phosphoranimine $BrMePhP{=}NSiMe_3$ (**11**)[11] [$\delta(^{31}P) = 4$ ppm] with a stoichiometric quantity of $(MeO)_3P$ in $CDCl_3$ after 3 h also revealed the quantitative generation of polymer **10** [$\delta(^{31}P) = 1.8$ ppm] by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy.[3b] The product was also isolated in high yield as a film-forming fibrous material by precipitation in pentane and was shown to possess a high molecular weight by gel permeation chromatography (GPC) versus polystyrene standards with a weight average molecular weight of 4.81×10^5 g/mol and a polydispersity index of 1.68. Repeating the above reaction with a substoichiometric (e.g., 0.1 molar equiv) amount of phosphite resulted in analogous polymerization chemistry (see Table 1).

Table 1. Molecular Weight Data for Polymer **10**

$(RO)_3P$	monomer/ phosphite (mol/mol)	solvent	time (h)	M_w ($\times 10^5$) (g/mol)[a]	PDI[b]
$(MeO)_3P$	1	$CDCl_3$	3	4.81	1.68
$(MeO)_3P$	10	$CDCl_3$	4	8.22	1.69
$(EtO)_3P$	1	$CDCl_3$	2	1.47	2.05
$(PhO)_3P$	1	$CDCl_3$	48	4.42	6.50
$(MeO)_3P$	1	THF	4	2.11	3.69
$(MeO)_3P$	1	toluene	8	1.48	1.94

[a] 0.1% $^tBu_4NBr$ (w/w) in THF eluent. Estimated versus polystyrene standards. [b] PDI = polydispersity index (M_w/M_n).

To test the variability of the polymerization process, we proceeded to perform the polymerization by employing different phosphites, such as $(EtO)_3P$ and $(PhO)_3P$, and different solvents, such as THF and toluene. High molecular weight polymer was obtained in all cases with the most significant difference between polymerizations being reaction time (Table 1).

In summary, we report the first P-donor-stabilized phosphoranimine cations from the reaction of phosphines and *N*-silyl-(halogeno)organophosphoranimines. The magnitudes of $^1J_{PP}$ present in these systems suggest a close association with an electronic push−pull mechanism. Remarkably, employing phosphites $(RO)_3P$ resulted instead in the generation of high molecular weight poly(alkyl/aryl)phosphazenes at ambient temperature. This unexpected route offers significant potential advantages over the usual thermal polycondensation route to poly(alkyl/aryl)phosphazenes which requires reaction temperatures of up to 190 °C under vacuum and reaction times in the order of days.[3] We are currently exploring the reactivity of the new P-donor-stabilized phosphoranimine cations and are also performing detailed studies which aim to elucidate the mechanism of polymerization.

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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) For example: (a) Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993; pp 403−483. (b) Steiner, A.; Zacchini, S.; Richards, P. I. *Coord. Chem. Rev.* **2002**, *227*, 193.
(2) For recent reviews, see: (a) Stephan, D. W. *Organometallics* **2005**, *24*, 2548. (b) Dehnicke, K.; Straehle, J. *Polyhedron* **1989**, *8*, 707.
(3) (a) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848. (b) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910−916. (c) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541. (d) Neilson, R. H.; Jinkerson, D. L.; Kucera, W. R.; Longlet, J. J.; Samual, R. C.; Wood, C. E. ACS Symposium Series 572; American Chemical Society: Washington, DC, 1994; p 232. (e) Walker, C. H.; St. John, J. V.; Wisian-Neilson, P. *J. Am. Chem. Soc.* **2001**, *123*, 3846.
(4) Montague, R. A.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1990**, *112*, 6721.
(5) Honeyman, C. H.; Manners, I.; Morrisey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035.
(6) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315.
(7) (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.
(8) Rivard, E.; Huynh, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 2286.
(9) (a) Niecke, E.; Bitter, W. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 127. (b) Wang, B.; Rivard, E.; Manners, I. *Inorg. Chem.* **2002**, *41*, 1690.
(10) (a) Burford, N.; Ragogna, P. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4307. (b) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 14404.
(11) Huynh, K.; Rivard, E.; LeBlanc, W.; Blackstone, V.; Lough, A. J.; Manners, I. *Inorg. Chem.* **2006**, *45*, 7922.
(12) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875.
(13) See Supporting Information for experimental details.
(14) The $^1J_{PP}$ values of singly bonded P(III)P(V) compounds are typically greater than 100 Hz: (a) Forgeron, M. A. M.; Gee, M.; Wasylishen, R. E. *J. Phys. Chem. A* **2004**, *108*, 4895. (b) Dixon, K. R. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 369−402.
(15) Gilheany, D. G. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: New York, 1990; Vol. 1, Chapter 2.
(16) For comparison, typical P=N phosphazene bond lengths range from 1.54 to 1.58 Å and P=N−R angles range from 119 to 143°: Allen, C. W. *Coord. Chem. Rev.* **1994**, *130*, 137.

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