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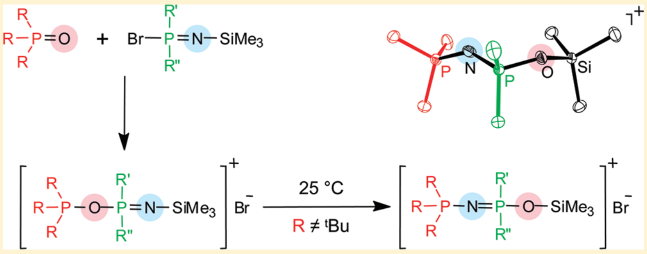
Reactions of Phosphine Oxides with Bromophosphoranimines; Synthesis and Unusual Rearrangements of O−Donor Stabilized Phosphoranimine Cations

Martin Bendle,[†] Keith Huynh,[‡] Mairi F. Haddow,[†] and Ian Manners*[,†]

[†]School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, U.K.

[‡]Department of Chemistry, University of Toronto, 80 Saint George Street, Toronto, Ontario M5S 3H6, Canada

S *Supporting Information*

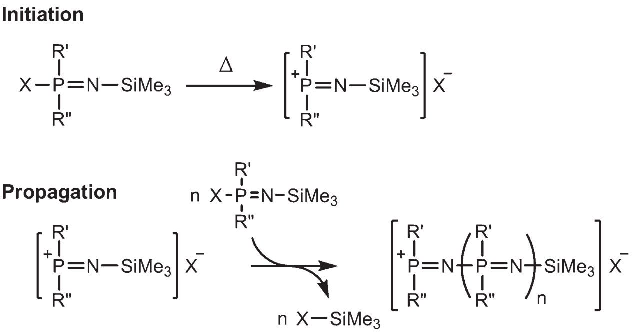


ABSTRACT: Reaction of phosphine oxides $R_3P{=}O$ [R = Me (**1a**), Et (**1c**), ${}^iPr$ (**1d**) and Ph (**1e**)], with the bromophosphoranimines $BrPR'R''P{=}NSiMe_3$ [R′ = R″ = Me (**2a**); R′ = Me, R″ = Ph (**2b**); R′ = R″ = OCH_2CF_3 (**2c**)] in the presence or absence of AgOTf (OTf = CF_3SO_3) resulted in a rearrangement reaction to give the salts $[R_3P{=}N{=}PR'R''O{-}SiMe_3]X$ (X = Br or OTf) ([**4**]X). Reaction of phosphine oxide **1a** with the phosphoranimine $BrPMe_2{=}NSiPh_3$ (**5**) with a sterically encumbered silyl group also resulted in the analogous rearranged product $[Me_3P{=}N{=}PMe_2O\text{-}SiPh_3]X$ ([**8**]X) but at a significantly slower rate. In contrast, the direct reaction of the bulky *tert*-butyl substituted phosphine oxide, ${}^tBu_3P{=}O$ (**1b**) with **2a** or **2c** in the presence of AgOTf yielded the phosphine oxide-stabilized phosphoranimine cations $[{}^tBu_3P{=}O{\cdot}PR'_2{=}NSiMe_3]^+$ ([**3**]$^+$, R′ = Me (**d**), OCH_2CF_3 (**e**)). A mechanism is proposed for the unexpected formation of [**4**]$^+$ in which the formation of the donor-stabilized adduct [**3**]$^+$ occurs as the first step.

INTRODUCTION

Phosphoranimines, $R_3P{=}NR'$ have a diverse chemistry and have been the subject of considerable attention in the field of main group chemistry.[1,2] *N*-Silylphosphoranimines ($XRR'P{=}NSiMe_3$, X = halogen, alkoxy; R, R′ = alkyl, aryl, aryloxy, and Cl) are of particular interest as precursors to form polyphosphazenes $[RR'P{=}N]_n$.[3−15] The use of these species as monomers complements the alternative ring-opening polymerization (ROP) approach from hexachlorocyclotriphosphazene $[Cl_2P{=}N]_3$ which affords polydichlorophosphazene, $[Cl_2P{=}N]_n$, at 200−250 °C[16,17] or at room temperature using trialkylsilylium carborane initiators.[18,19] For example, the PCl_5-catalyzed polymerization of $Cl_3P{=}NSiMe_3$ is a living process and provides access to $[Cl_2P{=}N]_n$ with molecular weight control and narrow polydispersities, compared to the broad molecular weight distributions afforded by the high temperature ROP of $[Cl_2P{=}N]_3$.[10,11,20−23] Moreover, although the ROP route yields a wide variety of polyphosphazenes with RO-, RN(H)-, and RR′N-substituents following nucleophilic replacement of the halogen groups in $[Cl_2P{=}N]_n$,[16,17,24−29] only partial substitution is possible with alkyl or aryl groups. This limitation is a consequence of the chain cleavage reactions that take place on treatment of $[Cl_2P{=}N]_n$ with Grignard or organolithium reagents,[17,30,31] but was overcome by the development of the thermal condensation polymerization of N-silyl phosphoranimines. This route yields poly(alkyl/aryl)phosphazenes through the use of *presubstituted* phosphoranimines, which can be synthesized with a wide range of alkyl and aryl groups.[3−6,8,9,12,32−36] The mechanism of this route has been tentatively proposed to involve formation of a highly reactive cationic phosphorus(V)−nitrogen species through heterolytic cleavage of a P-X (X = halogen, OR, R = alkyl, aryl) bond in the monomer to generate an active cation, $[RRP{=}NSiMe_3]^{+}$.[9] This highly Lewis acidic species would be expected to be reactive toward the monomer and initiate a chain-growth condensation polymerization of the phosphoranimine $CF_3CH_2OP(RR'){=}NSiMe_3$, at temperatures exceeding 200 °C (Scheme 1).

Scheme 1



The proposed intermediacy of cationic phosphoranimine species in the polymerization mechanism has made their generation and isolation of key relevance. Phosphoranimine cations of the form $[P(RR'){=}NSiMe_3]^+$ (R, R′ = halogen, alkyl, aryl,

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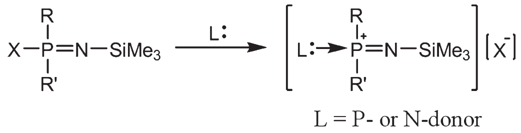
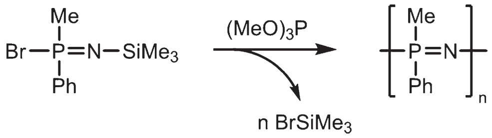
Scheme 2



Scheme 3



alkoxy) would be expected to be highly electrophilic, and are therefore likely to require significant stabilization by a suitable donor to permit their isolation (Scheme 2). Reaction of DMAP (4-dimethylaminopyridine) with $Cl_3P{=}NSiMe_3$ has been shown to afford the donor-stabilized cation $[DMAP\cdot PCl_2P{=}NSiMe_3]^+$.[37] This chemistry has been extended to a series of other nitrogen-donors, and substituted phosphoranimines, $XP(RR'){=}NSiMe_3$ (X = Cl, Br; R, R′ = Me, Ph, OCH_2CF_3),[37,38] as well as a DMAP-stabilized hexacationic cyclophosphazene synthesized from the reaction of DMAP with $[Cl_2P{=}N]_3$.[39] Attempts to transpose this chemistry to phosphines successfully gave the phosphine-stabilized cations, $[R''_3P{-}P(RR'){=}NSiMe_3]^+$ for a number of alkyl-, aryl-, and alkoxy-substituted phosphoranimines.[40,41] However, reaction of phosphines (R_3P, R = Me, Ph) with the trichloro-substituted phosphoranimine ($Cl_3P{=}NSiMe_3$) resulted in an unexpected dehalogenation reaction to give $R_3P{=}N{-}PCl_2$ via a complex mechanism that involves a number of reductive chlorination and condensation steps.[42]

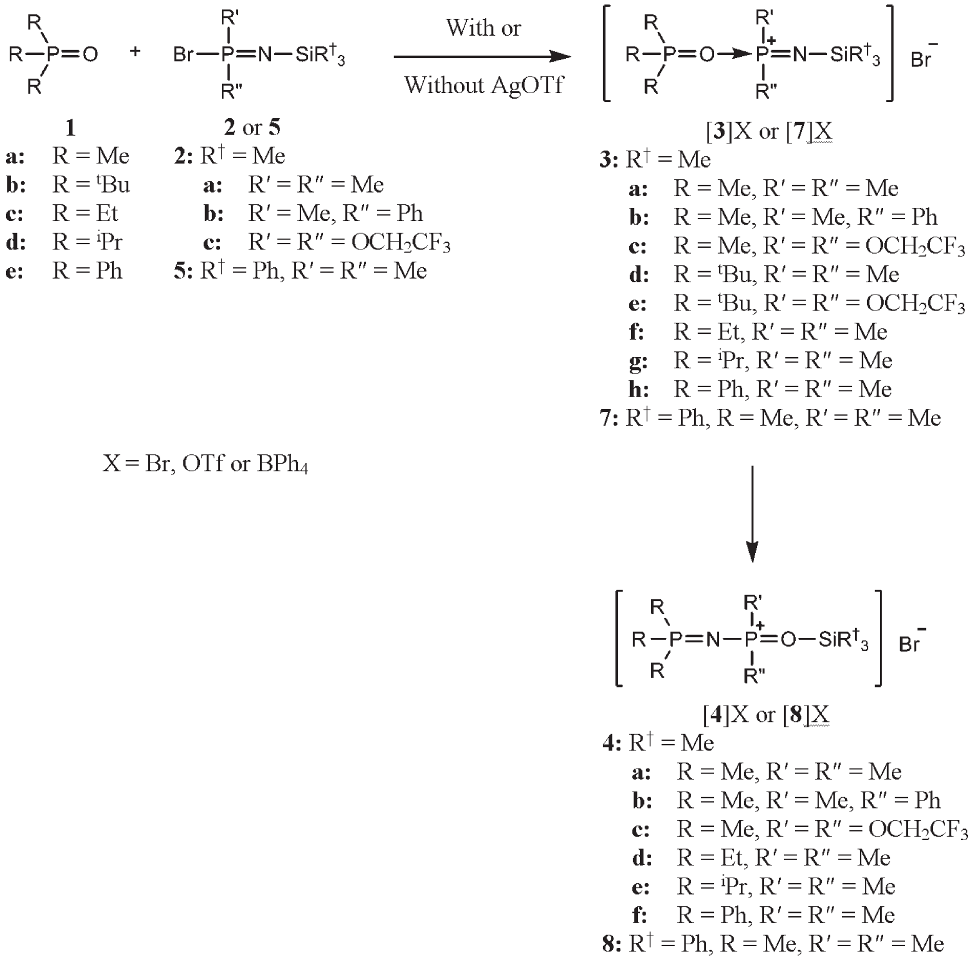
Interestingly, attempts to further diversify the chemistry to phosphite-stabilized cations via the reaction of the phosphoranimines $BrP(RR'){=}NSiMe_3$ (R = Me, R′ = Ph) with both stoichiometric and substoichiometric amounts of phosphite $(RO)_3P$ (R = Me, Et, Ph) at room temperature gave high molecular weight polymer $[RR'P{=}N]_n$ (M_w = 1.5−8.0 × 10^5 g mol^{-1}; PDI = 1.7−6.5) (for an example, see Scheme 3).[40,43] Our initial investigations into the mechanism of this reaction have revealed the presence of an induction period,[44] a result that poses intriguing questions as to the nature of the true catalyst or initiator in this system. There exists a possibility that a small amount of $BrSiMe_3$ (likely to be present as an impurity in the monomer) may act as a *co*-catalyst, reacting with the phosphite to give species bearing a P=O bond via an Arbuzov-type rearrangement reaction.[45,46] The product of such a reaction may be the true initiator. This has prompted us to investigate the reactions of phosphine oxides $R_3P{=}O$ with phosphoranimines to assess their ability to stabilize the phosphoranimine cations or act as polymerization initiators.[47] Herein we report our studies of the reactions of a series of phosphine oxides with phosphoranimines, which has led to the isolation of the targeted O-stabilized phosphoranimine cations as well as their participation in some unusual rearrangement reactions.

■ RESULTS AND DISCUSSION

1. Reactions of Phosphine Oxides (1a−e) with Bromophosphoranimines (2a−c). *(a). Reaction of* $Me_3P{=}O$ *(**1a**) with* $BrMe_2P{=}NSiMe_3$ *(**2a**).* Phosphine oxides $R_3P{=}O$ (**1**) were reacted with bromophosphoranimines (**2**), with the expectation that donor-stabilized cation salts [**3**]Br would be formed (Scheme 4), as has previously been observed for N- and P-donor ligands such as DMAP and PMe_3.[37,38,40,41] Indeed, when $BrMe_2P{=}NSiMe_3$ (**2a**) was reacted with 1 equiv of $Me_3P{=}O$ (**1a**) in CH_2Cl_2 for 10 min at 25 °C, $^{31}P\{^1H\}$ NMR revealed consumption of the starting materials and the formation of a new species (72% yield by $^{31}P\{^1H\}$ NMR integration) with resonances at δ = 35.7 and 95.0 ppm, $^2J_{PP}$ = 28.8 Hz, presumed to be the anticipated[48] cation $[\mathbf{3a}]^+$ (Scheme 1). However, in addition to the (initial) major product, several other species were also observed by $^{31}P\{^1H\}$ NMR (Figure 1). Moreover, the concentration of $[\mathbf{3a}]^+$ decreased after 60 min, and this was accompanied by the increase in concentration of a new product with resonances at δ = 25.0 and 40.9 ppm ($^2J_{PP}$ = 20.9 Hz). After 10 h, only trace quantities of the species giving rise to the initially observed resonances at δ = 35.7 and 95.0 ppm were present and after 5 d, 92% conversion to the product with two resonances at δ = 25.0 and 40.9 ppm was detected. Notably, no signal corresponding to poly(dimethylphosphazene) $[Me_2P{=}N]_n$ (δ_P = 8 ppm)[8] was observed. Purification of the product to allow isolation as a crystalline material was hindered by the presence of small quantities of impurities. To circumvent this problem, the reaction was repeated in the presence of 1 equiv of AgOTf to replace the anticipated Br^- counterion (precipitated as AgBr) in the product with $[OTf]^-$. $^{31}P\{^1H\}$ NMR of the filtered reaction mixture after 60 min showed complete consumption of starting materials, as well as the formation of all species observed in the aforementioned reaction without AgOTf. Interestingly, the exchange of the anion also resulted in a more rapid conversion of the initial product (presumed to be $[\mathbf{3a}]^+$) with $^{31}P\{^1H\}$ NMR resonances at δ = 37.3 and 94.0 ppm ($^2J_{PP}$ = 28.6 Hz) to the final product (δ = 25.0 and 39.8 ppm, $^2J_{PP}$ = 17.3 Hz) (72% yield after 60 min), with no significant increase in conversion beyond 96% after 24 h. Along with decrease in the reaction time, use of the triflate anion permitted isolation of the final product as a white crystalline solid allowing characterization of the product by single-crystal X-ray diffraction. Surprisingly, the X-ray study showed the product to be [**4a**]OTf, thereby suggesting that the targeted (and initially formed) cation $[\mathbf{3a}]^+$ had undergone a structural rearrangement (Figure 2, Scheme 4).

*(b). Reaction of **1a** with* $BrMePhP{=}NSiMe_3$ *(**2b**) and* $Br(CF_3CH_2O)_2P{=}NSiMe_3$ *(**2c**).* To gain insight into the scope of this unexpected rearrangement process we studied analogous reactions where the substituents on the phosphoranimine substrate were varied. The possibility that increased steric bulk might allow the stabilization of other intermediates during the rearrangement process led us to study the unsymmetrically substituted phosphoranimine $BrMePhP{=}NSiMe_3$ (**2b**) as a substrate. On reaction of **1a** and **2b** (25 °C, CH_2Cl_2), the resultant $^{31}P\{^1H\}$ NMR spectrum after 60 min revealed the formation of similar species to those formed in the reaction of **1a** with **2a** with comparable coupling constants and patterns, including resonances at δ = 24.0 and 95.7 ppm ($^2J_{PP}$ = 29.8 Hz), likely to be due to $[\mathbf{3b}]^+$, and a further species with resonances at δ = 28.5 and 29.1 ppm ($^2J_{PP}$ = 11.8 Hz), attributed to the rearranged product $[\mathbf{4b}]^+$ (Scheme 4). Complete consumption of $[\mathbf{3b}]^+$ was observed after 2 d and conversion to $[\mathbf{4b}]^+$ reached 89%, with no further change after 5 d. As for the reaction with **2a**, no resonances corresponding to polymer, $[MePhP{=}N]_n$ (δ_P = 1.8 ppm)[12,40] were detected. Repeating the reaction in the presence of 1 equiv of AgOTf, made no significant difference

Scheme 4



1
a: R = Me
b: R = ^{t}Bu
c: R = Et
d: R = ^{i}Pr
e: R = Ph

2 or **5**
2: R† = Me
a: R′ = R″ = Me
b: R′ = Me, R″ = Ph
c: R′ = R″ = OCH$_2$CF$_3$
5: R† = Ph, R′ = R″ = Me

[**3**]X or [**7**]X
3: R† = Me
a: R = Me, R′ = R″ = Me
b: R = Me, R′ = Me, R″ = Ph
c: R = Me, R′ = R″ = OCH$_2$CF$_3$
d: R = ^{t}Bu, R′ = R″ = Me
e: R = ^{t}Bu, R′ = R″ = OCH$_2$CF$_3$
f: R = Et, R′ = R″ = Me
g: R = ^{i}Pr, R′ = R″ = Me
h: R = Ph, R′ = R″ = Me
7: R† = Ph, R = Me, R′ = R″ = Me

X = Br, OTf or BPh$_4$

[**4**]X or [**8**]X
4: R† = Me
a: R = Me, R′ = R″ = Me
b: R = Me, R′ = Me, R″ = Ph
c: R = Me, R′ = R″ = OCH$_2$CF$_3$
d: R = Et, R′ = R″ = Me
e: R = ^{i}Pr, R′ = R″ = Me
f: R = Ph, R′ = R″ = Me
8: R† = Ph, R = Me, R′ = R″ = Me

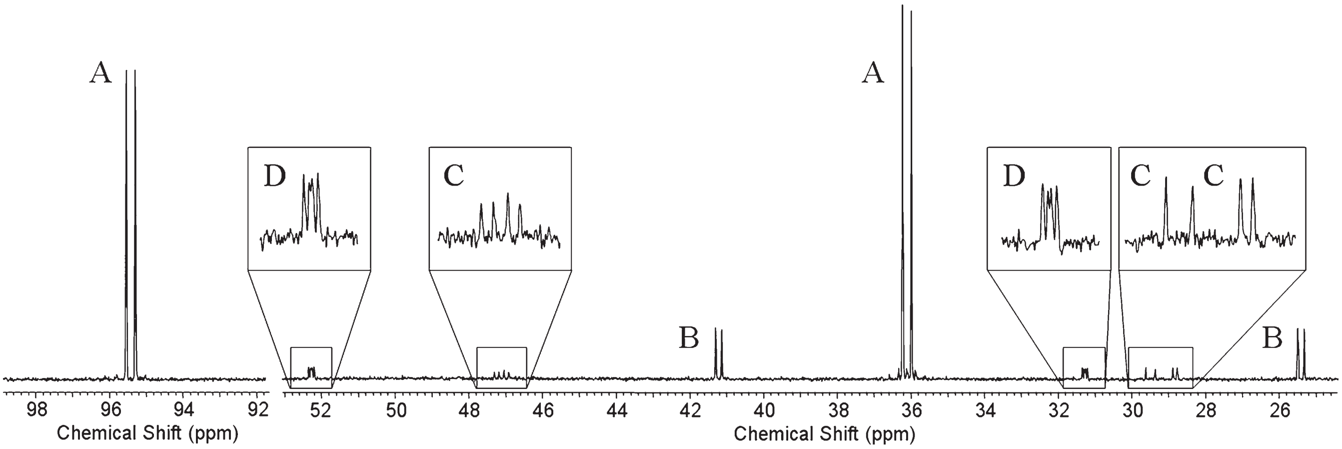


Figure 1. ^{31}P{^{1}H} NMR spectrum of the reaction between **1a** and **2a** in CH$_2$Cl$_2$ after 10 min. Signals A and B correspond to the cations [**3a**]$^+$ and [**4a**]$^+$ respectively, C and D were unidentified intermediates (see Supporting Information).

to the rate of the reaction, but did permit more complete conversion to [**4b**]$^+$ (ca. 100%) after 10 days.

To further investigate the effect of varying the phosphoranimine, Br(CF$_3$CH$_2$O)$_2$P=NSiMe$_3$ (**2c**) was also reacted with **1a**. The use of species **2c**, with particularly electron-withdrawing CF$_3$CH$_2$O substituents as a substrate, has previously been shown to afford a significant increase in the stability of the respective P- and N-donor stabilized cations compared to alkyl-substituted phosphoranimines.[38,41] ^{31}P{^{1}H} NMR analysis of the reaction of **1a** with **2c** (25 °C, CH$_2$Cl$_2$) after 60 min showed incomplete

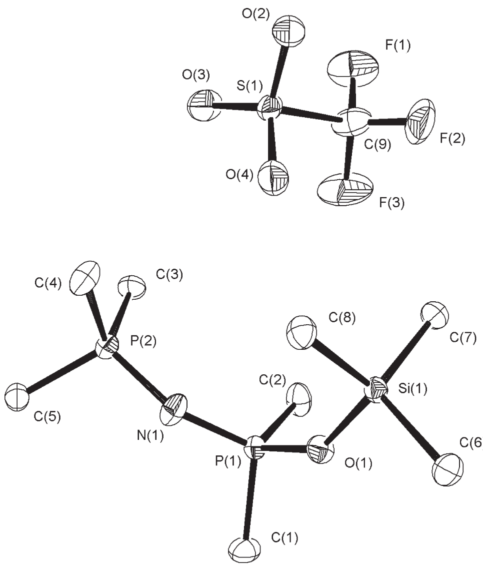


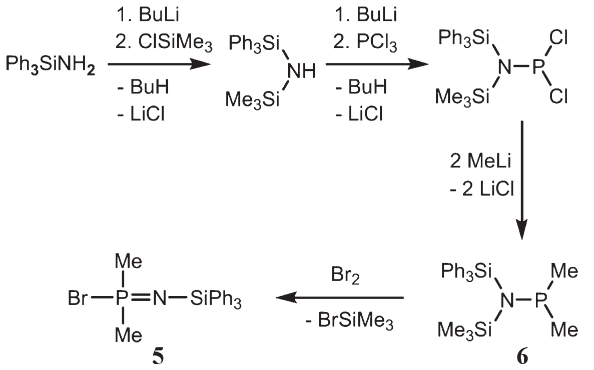
Figure 2. Thermal ellipsoid plot of [**4a**]OTf at the 50% probability level. All hydrogen atoms have been omitted for clarity.

consumption of starting materials, and formation of a new species with resonances consistent with the structure [**3c**]$^+$, δ = −26.3 (d, $^2J_{PP}$ = 32.0 Hz), 105.2 ppm (d, $^2J_{PP}$ = 32.0 Hz), and a species at δ = 2.5 (d, $^2J_{PP}$ = 23.7 Hz), 25.4 ppm (d, $^2J_{PP}$ = 23.7 Hz), presumed to be [**4c**]$^+$. Species [**3c**]$^+$ was no longer observed after 24 h, and the conversion to [**4c**]$^+$ increased to 83% after 10 days. Significant ^{31}P NMR peak broadening and the formation of inseparable oils on workup prompted us to repeat the reaction in the presence of a stoichiometric quantity of AgOTf. For similar reasons, the final product could not be purified.

*(c). Effect of Changing the Phosphoranimine Silyl Substituent; Synthesis and Reactivity of BrMe$_2$P=NSiPh$_3$ (**5**).* Next, we investigated the effect of replacing the SiMe$_3$ group on the phosphoranimine nitrogen center with the more bulky SiPh$_3$ analogue. On the basis of previous reactivity studies,[42,49,50] it was expected that this sterically encumbered phenyl-substituted silyl moiety might prevent or slow the rearrangement. We therefore prepared the new phosphoranimine, BrMe$_2$P=NSiPh$_3$ (**5**) via the oxidative bromination of the *N*-silylaminophosphine **6** with Br$_2$ in CH$_2$Cl$_2$ (Scheme 5). An X-ray crystallographic study was undertaken of the crystalline product which, along with multinuclear NMR, confirmed the formation of **5** (Figure 3).

The reaction of **1a** with **5** (25 °C, CH$_2$Cl$_2$) appeared analogous to the reaction of **1a** with the tri*methyl*silylphosphoranimine (**2a**), but with a significantly slower conversion to the final product of 66% after 5 d: a similar set of solution species, analogous to those observed in the reaction of **1a** and **2a** were identified by ^{31}P{^{1}H} NMR, including [**7**]$^+$ and [**8**]$^+$, the tri*phenyl*-substituted analogues of [**3a**]$^+$ and [**4a**]$^+$, respectively. Importantly, the formation of [**7**]$^+$ occurred at a similar rate to the formation of [**3a**]$^+$ from **2a** whereas the subsequent rearrangement to [**8**]$^+$ was a slower process compared to the conversion of [**3a**]$^+$ to [**4a**]$^+$. Performing the reaction of **1a** with **5** in the presence of AgOTf further slowed the reaction, with 45% conversion to [**8**]OTf after 5 d, but permitted isolation of the product in a form suitable for single-crystal X-ray diffraction. The result of the X-ray study and further multinuclear NMR analysis confirmed that the product, [**8**]OTf, was the analogue of [**4a**]OTf with SiPh$_3$ substituents in place of an SiMe$_3$ group at nitrogen (Scheme 4, Figure 4).

Scheme 5



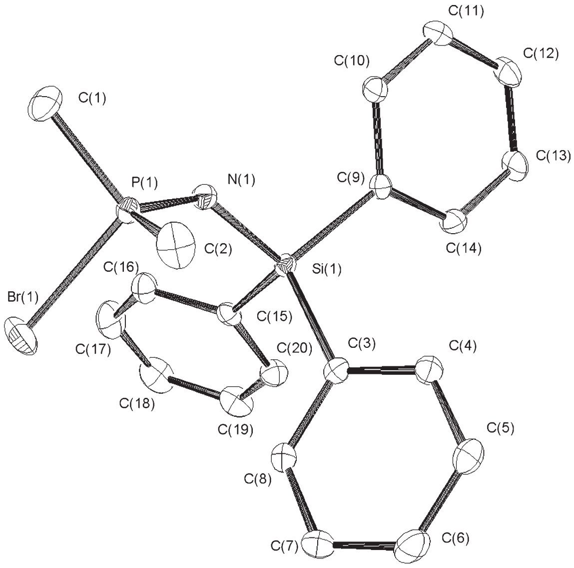


Figure 3. Thermal ellipsoid plot of **5** at the 50% probability level. All hydrogen atoms have been omitted for clarity.

*(d). Reaction of the Sterically Encumbered Phosphine Oxide, ^{t}Bu$_3$P=O (**1b**), with Phosphoranimines **2a** and **2c**.* Next, we investigated the analogous chemistry using a bulky phosphine oxide, ^{t}Bu$_3$P=O (**1b**) with the aim of isolating intermediates in the rearrangement reaction. Phosphoranimine **2a** was therefore treated with 1 equiv of **1b** (25 °C, CH$_2$Cl$_2$). Analysis of the reaction solution by ^{31}P{^{1}H} NMR after 10 min revealed about 2% conversion to a single product displaying two resonances (δ = 32.0 and 113.3 ppm, $^2J_{PP}$ = 66.3 Hz). On the basis of the similar shifts and an increase in the coupling constant (attributed to the stronger P=O→P$^+$ interaction afforded by the more strongly electron donating phosphine oxide), this product appeared analogous to the intermediate [**3a**]$^+$ formed in the reaction of **1a** with **2a** (with resonances at δ = 35.7 and 95.0 ppm, $^2J_{PP}$ = 28.8 Hz). However, no further reaction beyond 5% was observed between **1b** and **2a** after 40 min. This was presumed to be a result of an equilibrium resulting from competitive nucleophilic attack of the bromide counterion to displace the sterically encumbered phosphine **1b**. Similar equilibria have been previously detected for the formation of P- and N-donor stabilized phosphoranimine

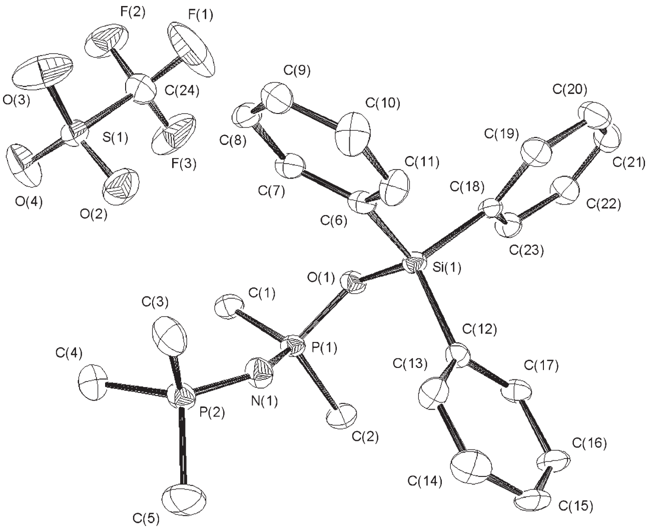


Figure 4. Thermal ellipsoid plot of [**8**]OTf at the 50% probability level. All hydrogen atoms have been omitted for clarity.

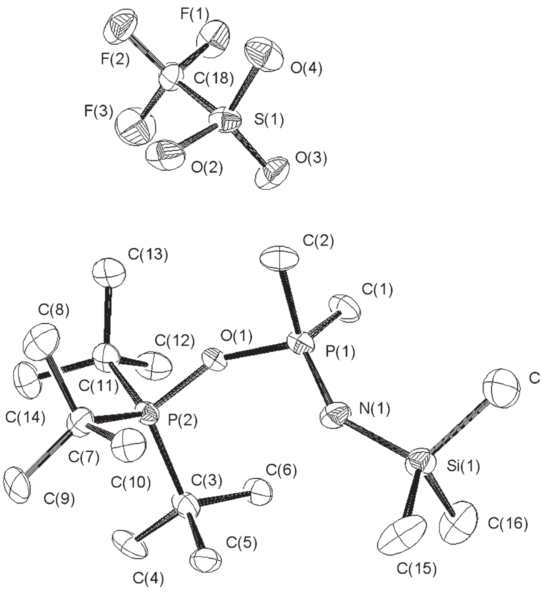


Figure 5. Thermal ellipsoid plot of [**3d**]OTf at the 50% probability level. All hydrogen atoms have been omitted for clarity.

cations from the free donor ligand and the halogenophosphoranimine substrate.[38,41]

To drive the equilibrium in favor of $[\mathbf{3d}]^+$ the reaction was repeated in the presence of 1 equiv of AgOTf to facilitate the removal of the bromide counterion as AgBr. As anticipated, $^{31}P\{^1H\}$ NMR analysis of the reaction mixture formed by **1b** and **2a** in the presence of 1 equiv of AgOTf after 16 h showed the quantitative formation of a single species with no significant differences in shift and coupling constants compared to the product of the reaction in the absence of the silver salt. After workup and recrystallization, the product was confirmed to be the phosphine oxide-stabilized phosphoranimine salt [**3d**]OTf (Scheme 4) by X-ray diffraction (Figure 5).

In light of this result, we attempted to explore the generality of this reaction with respect to other phosphoranimine substrates.

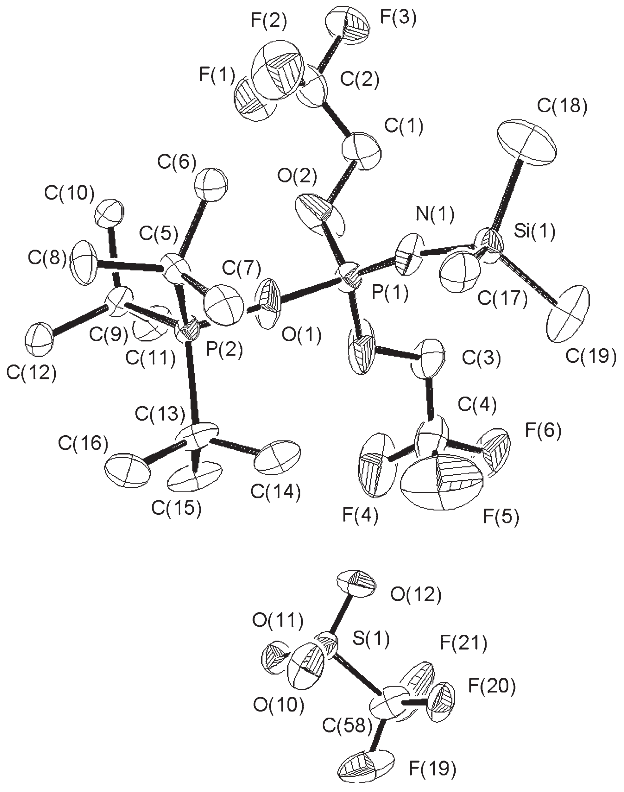


Figure 6. Thermal ellipsoid plot of [**3e**]OTf at the 50% probability level. All hydrogen atoms and additional molecules in the asymmetric unit have been omitted for clarity.

Reaction of 1 equiv of **1b** with the trifluoroethoxy-substituted phosphoranimine $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**2c**) (25 °C, CH_2Cl_2) in the presence of 1 equiv of AgOTf also yielded a single product by $^{31}P\{^1H\}$ NMR after 16 h with δ = 30.5 (d, $^2J_{PP}$ = 67 Hz), 118.6 ppm (d, $^2J_{PP}$ = 67 Hz). This species was also isolated and characterized as an O-donor-stabilized salt of a phosphoranimine cation [**3e**]OTf by single crystal X-ray diffraction (Figure 6, Scheme 4).

*(e). Reaction of $R_3P{=}O$ (R = Et, ^{i}Pr, Ph, **1c**−**e**) with Phosphoranimine $BrMe_2P{=}NSiMe_3$ (**2a**).* To examine the scope of the reaction beyond Me- and ^{t}Bu-substituted phosphine oxides, $Et_3P{=}O$ (**1c**), $^iPr_3P{=}O$ (**1d**), and $Ph_3P{=}O$ (**1e**) were also reacted with **2a**. We hoped that the range of steric and electronic properties intrinsic to **1c**−**e** would allow us to identify one or more of the other intermediates in the observed rearrangement process. Reaction of **1c** with **2a** (25 °C, CH_2Cl_2) appeared to proceed similarly to that observed between **1a** and **2a**, with the observation of comparable resonances by $^{31}P\{^1H\}$ NMR and 85% conversion to $[\mathbf{4d}]^+$ after 5 d. This suggested that the increase in steric bulk from Me to Et was not sufficient to afford any significant stabilization of the initial adduct, $[\mathbf{3f}]^+$, or any of the other potential intermediate species in the reaction pathway. The rearrangement was confirmed by repeating the reaction with 1 equiv of AgOTf (which gave a slight decrease in rate), and this led to the isolation [**4d**]OTf, which was characterized by multinuclear NMR and single crystal diffraction (Figure 7).

Reaction of **1d** with **2a** (25 °C, CH_2Cl_2) also preceded as for **1a** and **1c**, but with an apparent equilibrium between the starting materials and initial adduct $[\mathbf{3g}]^+$. A second set of resonances, consistent with the formation of the rearranged product ([**4e**]$^+$, comprising 4% of phosphorus-containing species) was observed by ^{31}P{^{1}H} NMR after 1 h. Further monitoring showed 24% conversion to [**4e**]$^+$ after 5 d, but at a rate slower than apparent side reactions to afford unidentified products. Repeating the reaction between **1d** and **2a** in the presence of 1 equiv of AgOTf gave almost quantitative conversion of starting materials to [**3g**]$^+$ after 1 h, but appeared to further slow the subsequent formation of [**4e**]$^+$ with only about 2% conversion after 5 d.

In the reaction of **1e** with **2a** (25 °C, CH_2Cl_2) the consumption of starting materials was very slow with only 4% conversion to [**4f**]$^+$ after 5 days, but no resonances that could indicate the formation of [**3h**]$^+$ were observed, despite detection of small amounts of other species analogous to those observed in the reaction of **1a** with **2a**. This could be explained by the bulky nature and poor donor ability of **1e** which would disfavor the formation of [**3h**]$^+$ with Br$^-$ as the counteranion. When the reaction of **1e** with **2a** was repeated in the presence of 1 equiv of AgOTf for 1 h, the resultant ^{31}P{^{1}H} NMR showed complete consumption of starting materials after 1 h to give 47% [**3h**]$^+$ and 44% [**4f**]$^+$, with [**3h**]$^+$ no longer observed after 10 h, and conversion to [**4f**]$^+$ maximizing at 91% after 24 h. This faster conversion (44% in 1 h compared to 4% in 5 d without AgOTf) supported the hypothesis that [**4**]$^+$ was formed from [**3**]$^+$ with the resultant overall rate of the rearrangement reaction dependent on the concentration of [**3**]$^+$.

These results show that **1c**−**e** exhibit reactivities toward phosphoranimine **2a** that are in-between those of **1a** and **1b**, with rates of rearrangement from [**3**]$^+$ to [**4**]$^+$ decreasing with increasing size of the phosphine oxide substituents. Equilibria were also observed between the starting materials and [**3**]$^+$ for the sterically more demanding phosphine oxides **1b** and **1d**, presumably because of unfavorable interactions which favor significant phosphine oxide loss from [**3**]$^+$ and the recoordination of Br$^-$.

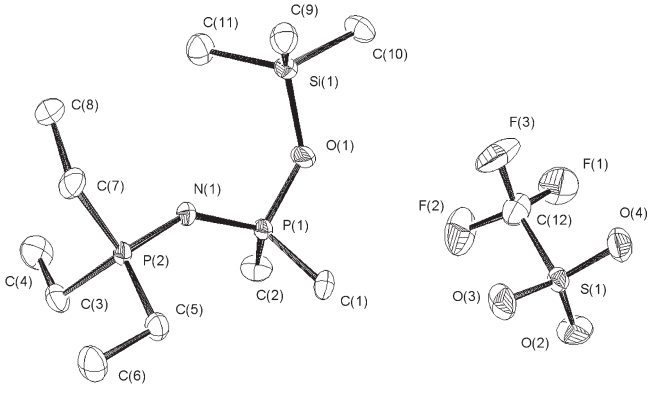


Figure 7. Thermal ellipsoid plot of [**4d**]OTf at the 50% probability level. All hydrogen atoms have been omitted for clarity.

The adduct [**3**]$^+$ was also further destabilized when the phosphine oxide possessed relatively electron withdrawing phenyl groups (**1e**).

2. Discussion of X-ray Crystallographic and NMR Characterization Data for O−Donor Stabilized Cations [3]$^+$ and Rearranged Cations [4]$^+$. *(a). Structural Characterization of the Phosphine Oxide-Stabilized Phosphoranimine Cations [**3**]$^+$.* Selected examples of the cations [**3**]$^+$ were studied by X-ray crystallography (Tables 1 and 2) and confirmed the reported atom connectivity. Selected bond lengths and angles for the O-donor stabilized cations [**3**]$^+$ are given in Table 1 (see also Tables 2 and 3). The P(2)−O(1) distances show no significant variation, suggesting that the phosphine oxide P−O bond length was relatively insensitive to changes in substituents on the phosphoranimine. The O−P(1) distance was found to be more sensitive to substituent variation, with the bond length in [**3d**]$^+$ (1.641(4) Å) being significantly greater than for [**3e**]$^+$

Table 2. Crystal Data and Structural Refinement for [3d]OTf, [3e]OTf, and 5

	[**3d**]OTf	[**3e**]OTf	**5**
empirical formula	$C_{18}H_{42}F_3$-NO_4P_2SSi	$C_{20}H_{40}F_9$-NO_6P_2SSi	$C_{20}H_{21}$-BrNPSi
formula weight	515.62	683.62	414.35
crystal system	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/c$	*Cc*
a (Å)	9.2967(3)	24.9510(12)	16.395(2)
b (Å)	17.1918(7)	17.4531(8)	9.2190(12)
c (Å)	33.2588(12)	22.1048(9)	13.7655(17)
α (deg)	90	90	90
β (deg)	90	93.280(2)	105.461(6)
γ (deg)	90	90	90
V (Å^3)	5315.7(3)	9610.3(7)	2005.3(4)
Z	8	12	4
D_C (mg m^{-3})	1.289	1.417	1.372
μ (Mo Kα), mm^{-1}	0.331	0.324	2.191
F(000)	2208	4272	848
θ range (deg)	2.37−24.76	2.17−24.88	2.56−23.12
index ranges	$-10 \le h \le 11$	$-30 \le h \le 27$	$-23 \le h \le 23$
	$-20 \le k \le 18$	$-21 \le k \le 21$	$-13 \le k \le 13$
	$-40 \le l \le 32$	$-18 \le l \le 26$	$-19 \le l \le 19$
reflns colled	25295	72757	5427
independent	4867	17598	5427
temp (K)	100(2)	100(2)	100(2)
GOF on F^2	1.093	1.077	1.056
R, % ($I > 2\sigma[I]$)^a	6.93	10.28	2.49
R_w, %^{b}	16.03	25.40	6.33
peak/hole (e/Å^3)	0.469/−0.540	1.403/−0.580	0.453/−0.373

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$.

Table 1. Selected Bond Lengths and Angles for the Phosphine Oxide-Stabilized Phosphoranimine Salts [3d]OTf and [3e]OTf, $R_3P(2){-}O{-}P(1)R'R''{=}N{-}SiMe_3$

	P(2)−O(1) [Å]	O(1)−P(1) [Å]	P(1)=N(1) [Å]	N(1)−Si(1) [Å]	P(2)−O(1)−P(1) [deg]	P(1)−N(1)−Si(1) [deg]
[**3d**]OTf	1.571(4)	1.641(4)	1.523(5)	1.687(5)	153.0(3)	145.8(3)
[**3e**]OTf	1.584(5)	1.586(5)	1.471(7)	1.696(7)	159.7(5)	170.0(5)
	1.580(5)	1.564(5)	1.466(7)	1.710(7)	174.4(4)	162.0(5)
	1.568(5)	1.574(5)	1.481(7)	1.684(7)	176.6(5)	168.6(5)

^{a} Structural parameters for [**3e**]OTf are given for all three molecules in the asymmetric unit.

Table 3. Crystal Data and Structural Refinement for [4a]OTf, $[4a]PF_6$, [4d]OTf, and [8]OTf

	[**4a**]OTf	[**4a**]PF_6	[**4d**]OTf	[**8**]OTf
empirical formula	$C_9H_{24}F_3NO_4P_2SSi$	$C_8H_{24}F_6NOP_3Si$	$C_{12}H_{30}F_3NO_4P_2SSi$	$C_{24}H_{30}F3NO_4P_2SSi$
formula weight	389.38	385.28	431.46	575.58
crystal system	triclinic	monoclini	orthorhombic	monoclinic
space group	$P\bar{1}$	$C2/c$	$Pbca$	$P2_1/c$
a (Å)	8.3809(3)	13.9242(17)	13.8576(12)	18.5098(19)
b (Å)	8.7810(4)	10.7663(14)	13.4460(13)	9.7109(8)
c (Å)	13.9100(6)	24.733(3)	23.067(2)	16.3446(15)
α (deg)	73.781(2)	90	90	90
β (deg)	76.827(2)	104.734(2)	90	107.282(6)
γ (deg)	76.643(2)	90	90	90
V (Å^3)	941.61(7)	3585.8(8)	4298.0(7)	2805.3(5)
Z	2	8	8	4
D_C (mg m^{-3})	1.373	1.427	1.334	1.363
μ (Mo Kα), mm^{-1}	0.443	0.448	0.395	0.322
F(000)	408	1600	1824	1200
θ range (deg)	2.54−32.05	2.42−27.51	2.30−27.61	2.30−7.39
index ranges	$-12 \leq h \leq 12$	$-18 \leq h \leq 11$	$-18 \leq h \leq 18$	$-22 \leq h \leq 21$
	$-12 \leq k \leq 12$	$-13 \leq k \leq 13$	$-8 \leq k \leq 17$	$0 \leq k \leq 11$
	$0 \leq l \leq 20$	$-32 \leq l \leq 32$	$-30 \leq l \leq 30$	$0 \leq l \leq 19$
reflns colled	5936	15927	51399	4445
independent	5936	4111	4993	4445
temp (K)	100(2)	100(2)	100(2)	100(2)
GOF on F^2	1.073	1.029	1.060	1.149
R, % ($I > 2\sigma[I]$)^a	4.21	3.91	2.88	4.89
R_w, %^{b}	10.73	10.19	8.15	13.27
peak/hole (e/Å^3)	0.682/-0.831	1.013/-0.796	0.619/-0.251	0.370/-0.496

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.


A B

Figure 8. Resonance structures for $[3]^+$.

(1.564(5)−1.586(5) Å), suggesting that a stronger interaction between the phosphine oxide and the phosphoranimine was present in the latter case. This could be easily explained by the presence of the more electron-withdrawing OCH_2CF_3 substituents (compared to Me) creating an increased electron deficiency at the phosphoranimine phosphorus center and inducing a stronger bond between the phosphine oxide and the phosphoranimine phosphorus. In the case of [**3d**]$^+$ the O(1)−P(1) bond was longer than the P(2)−O(1) bond (1.641(5) vs 1.571(4) Å), supporting the bonding model of a formally phosphine oxide oxygen lone pair donating to the cationic phosphorus center (structure B, Figure 8). By contrast, in [**3e**]$^+$ these bonds were approximately the same length, suggesting that the interactions between both phosphorus centers and the phosphine oxide oxygen were more equivalent, and implying that the bonding arrangement was closer to that of structure A in Figure 8.

The phosphoranimine P═N bond lengths in the phosphine oxide-stabilized cations, $[3]^+$ (1.466(7)−1.523(5) Å) were shorter than the typical values (1.54−1.58 Å),[51] particularly in the case of [**3e**]$^+$, and were comparable to those observed for the N-donor (1.47−1.53 Å)[38,52] and phosphine-donor (1.48−1.53 Å)[41] stabilized phosphoranimine cations previously reported. This could be explained by a negative hyperconjugation interaction,[53] whereby an increased donation of the nitrogen lone-pairs into the σ^* orbitals of the phosphoranimine P−OR′ bonds was induced by the more electron-withdrawing substituents in [**3e**]$^+$. This may also explain the wider bond angle at N and O observed for [**3e**]$^+$ (162.0(5)−170.0(5)° and 159.7(5)−176.6(5)°, respectively) compared to [**3d**]$^+$ (145.8(3)° and 153.0(3)°), resulting from the presence of less stereochemically active lone pairs because of involvement in overlap with the empty phosphorus-substituent σ^* orbitals.

*(b). Structural Characterization of the Rearranged Cationic Products [**4**]$^+$.* X-ray studies were performed on several examples of salts of the cations [**4**]$^+$ (Tables 3 and 4). Selected bond lengths and angles for the rearranged cations ([**4**]$^+$ and [**8**]$^+$) are given in Table 4, including [**4a**]PF_6 (see Figure 10), isolated from the reaction of **1a** and **2a** in the presence of 1 equiv of $AgPF_6$. In all of the salts listed in Table 4, the P(2)−N(1) bond lengths (1.570(4)−1.5876(17) Å) were consistently elongated when compared to the P(1)−N(1) bond lengths (1.555(4)−1.5670(17) Å), and all possess bond lengths in the range for phosphorus−nitrogen double-bonds (1.54 to 1.58 Å).[51] This suggested that the positive charge was distributed between both phosphorus atoms within the P−N−P moiety (as is generally observed in the $[R_3P═N═PR_3]^+$ cations)[51] and therefore, that structures A and B (Figure 9) both contribute to the bonding description of [**4**]$^+$, but the weighting of B is larger. Although the

Table 4. Selected Bond Lengths and Angles for the Rearranged Salts [4a]OTf, [4a]PF$_6$^{a}, [4d]OTf, and [8]OTf, [$R_3P(2)$-N=P(1)R′R″-O-SiR$^†_3$]X

	P(2)−N(1) [Å]	N(1)−P(1) [Å]	P(1)−O(1)[Å]	O(1)−Si(1) [Å]	P(2)−N(1)−P(1) [deg]	P(1)−O(1)−Si(1) [deg]
[**4a**]OTf	1.580(2)	1.561(2)	1.5597(17)	1.6806(17)	145.35(16)	144.77(12)
[**4a**]PF$_6$	1.5876(17)	1.5670(17)	1.5615(16)	1.6623(16)	137.74(12)	153.77(12)
[**4d**]OTf	1.5838(11)	1.5605(11)	1.5607(10)	1.6738(10)	140.86(8)	137.11(6)
[**8**]OTf	1.570(4)	1.555(4)	1.578(3)	1.678(3)	146.2(3)	131.8(2)

[a] Synthesized in an analogous reaction to [**4a**]OTf, see Figure 10.

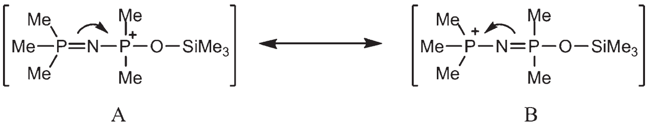


Figure 9. Resonance structures for [**4**]$^+$.

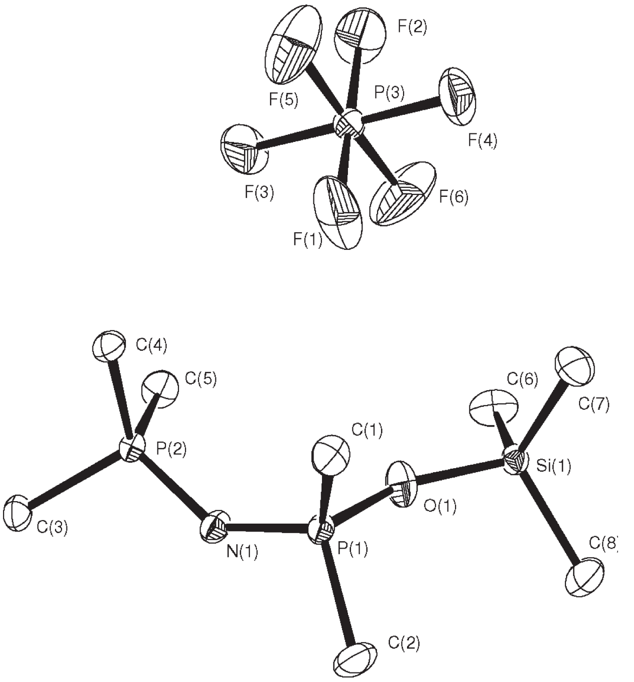
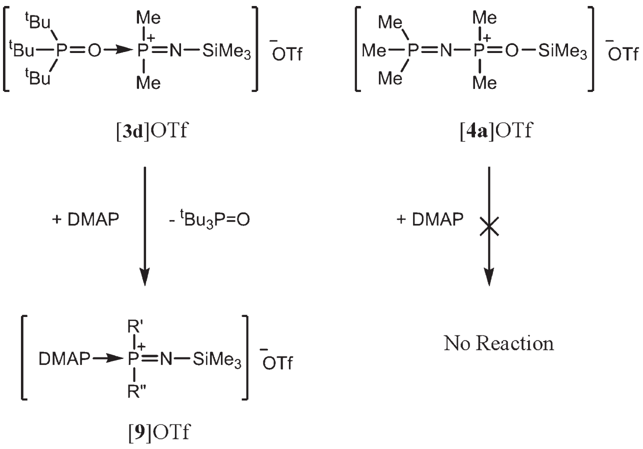


Figure 10. Thermal ellipsoid plot of [**4a**]PF$_6$ at the 50% probability level. All hydrogen atoms have been omitted for clarity.

P−N−P and P−O−Si bond angles show considerable variation, there appeared to be similar (P−O−Si) or greater (P−N−P) sensitivity to the crystal packing (from a change in counterion), than to a change in substituents on the silyl- or terminal phosphorus-groups. This result indicated that the bond angles at O and N were relatively flexible, and their solid-state geometric parameters were not a reliable indicator of any variation in bonding character for these species.

*(c). NMR Data for O-Stabilized Cationic Phosphoranimines ([**3**]$^+$) and Rearranged Products ([**4**]$^+$).* Multinuclear NMR analysis provided complementary evidence for the formulation of the cationic products as the donor-stabilized phosphoranimine cations [**3**]$^+$ and [**7**]$^+$, or rearranged products [**4**]$^+$ and [**8**]$^+$. Analysis of coupling interactions between various nuclei supported the assignments (vide supra): observed $^{31}P\{^1H\}$ NMR P−P couplings were generally greater for [**3**]$^+$ and [**7**]$^+$ (28.8 to 66.6 Hz) than for rearranged cations [**4**]$^+$ or [**8**]$^+$ (9.9 to 33.7 Hz). The values for [**3**]$^+$ and [**7**]$^+$ were also always significantly larger than for [**4**]$^+$ or [**8**]$^+$ when the substituents at P and Si were the same. In a number of examples it was also possible to observe $^2J_{SiP}$ couplings by both $^{31}P\{^1H\}$ NMR (as satellites) and $^{29}Si\{^1H\}$ NMR, allowing an assignment of the two ^{31}P resonances as either internal or terminal.

Scheme 6

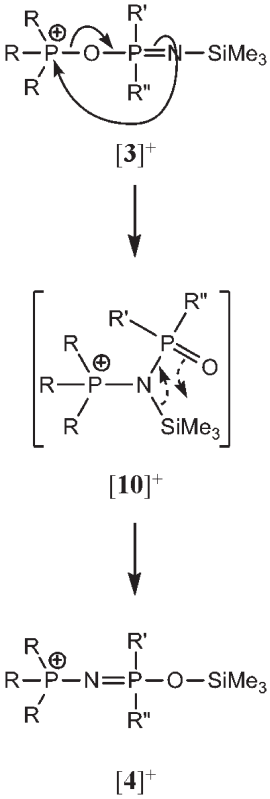


The variations in chemical shifts between [**3**]$^+$ or [**7**]$^+$ and [**4**]$^+$ or [**8**]$^+$ were also informative: from $^{31}P\{^1H\}$ NMR the P=O-stabilized phosphoranimine cations [**3**]$^+$ and [**7**]$^+$ all possess a ^{31}P resonance at high field (−30.9 to 41.4 ppm, attributed to the phosphoranimine phosphorus) and one at low field (58.7 to 118.5 ppm) for the O-donor phosphorus center. In contrast, the rearranged cations ([**4**]$^+$ and [**8**]$^+$) possess two $^{31}P\{^1H\}$ NMR resonances at a comparatively similar chemical shift (17.3 to 42.9 ppm).

The ^{29}Si NMR resonance attributed to the SiR_3 group in the isolated compounds also showed a strong sensitivity to the element to which it was bound (N or O). ^{29}Si NMR resonances were observed with negative chemical shift values (−26.5 to −3.8 ppm) when attached to a nitrogen atom of a phosphoranimine (**2**) or phosphoranimine cation ([**3**]$^+$),[38] while the rearranged product ([**4**]$^+$) showed a positive shift at significantly lower field (24.9 to 24.7 ppm), when attached to an oxygen atom.

3. Reactivity of Phosphine Oxide-Stabilized Cations [3]$^+$ and Rearranged Cations [4]$^+$. *(a). Reactions of [**3d**]$^+$ and [**4a**]$^+$ with DMAP.* The possible involvement of cations of type [**3**]$^+$ and [**4**]$^+$ in the phosphite-initiated polymerization of phosphoranimines $XR_2P=NSiMe_3$ (X = Cl or Br) prompted us to explore some key aspects of their chemistry. The structures of [**3**]$^+$ and [**4**]$^+$ suggested that the former would be expected to react with

Scheme 7



strongly donating ligands such as DMAP to displace the more weakly bound $R_3P{=}O$ ligand whereas the latter should display different reactivity.[38] Samples of [**3d**]OTf and [**4a**]OTf were each treated with a 2-fold excess of DMAP in solution at 25 °C. Reaction of [**3d**]OTf (prepared in situ in $CDCl_3$) with DMAP led to complete conversion to the DMAP-stabilized phosphoranimine cation $[\mathbf{9}]^+$,[38] and the release of 1 equiv of **1b** was detected by $^{31}P\{^1H\}$ and ^1H NMR. In contrast, a solution of [**4a**]OTf and a 2-fold excess of DMAP showed no reaction after 4 days, or when heated to 160 °C with 1 equiv of DMAP (Scheme 6).

(b). Thermal Stability of $[\mathbf{3d}]^+$ and Reactivity of $[\mathbf{3d}]^+$ and $[\mathbf{4a}]^+$ toward $BrMePhP{=}NSiMe_3$. Given that variation of the phosphine oxide or phosphoranimine substituents failed to permit isolation of any intermediates in the rearrangement of $[3]^+$ to form $[4]^+$, the reactivity of $[\mathbf{3d}]^+$ was explored at elevated temperature. However, when [**3d**]OTf was heated at 60−150 °C in 1,2-dichlorobenzene decomposition to uncharacterized products was detected by $^{31}P\{^1H\}$ NMR.

We also explored whether either of the cations of type $[3]^+$ and $[4]^+$ would function as initiators for the polymerization of the phosphoranimine $BrMePhP{=}NSiMe_3$ (**2b**). Reaction of [**4a**]OTf with a 10-fold excess of **2b** in 1,2-dichlorobenzene resulted in 42% conversion to a number of unidentified species after 14 h at 60 °C by $^{31}P\{^1H\}$ NMR. Complete decomposition was observed after heating to 160 °C for 5 h, but no ^{31}P NMR resonances that could be assigned to the formation of $[MePhP{=}N]_n$ (δ_P = 1.8 ppm)[12,40] were detected. Reaction of [**3d**]OTf with a 10-fold excess of **2b** in 1,2-dichlorobenzene at 25 °C only resulted in 98% conversion of the former to a new species observed by $^{31}P\{^1H\}$ NMR with two resonances at δ = 24.1 and 114.7 ppm ($^2J_{PP}$ = 67.7 Hz) and release of **2a** (δ = 6.9), presumably because of formation of the cation $[{}^tBu_3P{=}O{\rightarrow}PMePh{=}NSiMe_3]^+$. Heating the solution to 60 °C gave no further reaction, and raising the temperature to 160 °C resulted in decomposition, but with no $^{31}P\{^1H\}$ NMR evidence for the formation of $[MePhP{=}N]_n$ after redissolution of the nonvolatile products in $CDCl_3$.

4. Mechanistic Studies of the Rearrangement of $[3]^+$ to $[4]^+$. The transformation of $[3]^+$ to $[4]^+$ is mechanistically intriguing, with the rearrangement requiring connectivity transformations from $P{-}N{-}SiR_3$ to $P{-}O{-}SiR_3$ and from $R_3P{=}O{-}P$ to $R_3P{-}N{-}P$. A number of examples of reactions involving similar Me_3Si group migrations have been reported and are clearly relevant to the rearrangement from $[3]^+$ to $[4]^+$.[54−56] In these reports, an initially formed species containing a $P({=}O){-}NR'{-}SiR_3$ moiety rearranges to give the corresponding $R'N{-}P{-}O{-}SiR_3$ connectivity. In some of these examples, an intermolecular reaction involving a [1,3]-silyl migration is proposed; however, experimental evidence supporting this mechanism is limited. Although we have not been able to fully elucidate the mechanism for the conversion of $[3]^+$ to $[4]^+$ some important observations have been made that give useful information and allow us to tentatively propose a mechanism for this process.

(a). Influence of the Counterion in the Rearrangement of $[\mathbf{3}]^+$ to $[\mathbf{4}]^+$. We obtained results that allowed a comparison of the rates of rearrangement from $[\mathbf{3a}]^+$ to $[\mathbf{4a}]^+$ as a function of the counteranions of varying nucleophilicity (Br^-, $[OTf]^-$ and $[BPh_4]^-$). This was achieved by addition of a stoichiometric amount of the respective silver salt (AgX, X = OTf or BPh_4) to a 1:1 mixture of **1a** and **2a** (25 °C, CH_2Cl_2). This gave the immediate precipitation of a white solid (AgBr) along with complete consumption of **1a** and **2a** observed by $^{31}P\{^1H\}$ NMR. The reaction was also performed in the absence of added Ag salt and also in the presence of 5 equiv of $[Ph_4P]Br$ to provide further comparisons. These anion variations had a significant influence on the rates of both the consumption of $[\mathbf{3a}]^+$ and the formation of $[\mathbf{4a}]^+$. A faster rate of consumption of $[\mathbf{3a}]^+$ was generally observed for the less coordinating anions with the rate for the consumption fastest for $[BPh_4]^-$ and $[OTf]^-$ compared to Br^- and the case of excess Br^-, with 3%, 16%, 38%, and 47% of $[\mathbf{3a}]^+$ remaining, respectively, after 1 h. However, the significant slowing of the rearrangement for the reaction of **2a** with the bulky phosphine oxide **1d** (and between **1a** and **5** where the latter has a bulky silyl group) on exchanging the bromide counterion for triflate suggested the influence of the anion on the rearrangement was complex.

*(b). Effect of Varying the Phosphine Oxide (**1**) on the Rearrangement of $[\mathbf{3}]^+$ to $[\mathbf{4}]^+$.* With the exception of the highly sterically encumbered phosphine oxide **1b** (which did not form $[4]^+$) all of the phosphine oxides with smaller and less electron donating substituents (**1a,c-e**) formed $[3]^+$ on reaction with **2a**, which then apparently subsequently rearranged to $[4]^+$. Consideration of the rates of these reactions (when triflate was used as the counteranion to ensure a high initial conversion to $[\mathbf{3h}]^+$) allowed for a number of interesting observations. For the series of reactions of **1a**−**1e** with **2a** it was clear that the rate of rearrangement was sensitive to the nature of the substituent on the phosphine oxide. There was a significant decrease in rate as the size and electron donating capability of phosphine oxide substituents increased (92%, 18%, and 0% conversion to $[4]^+$ after 5 h for **1a**, **1c**, and **1d** respectively, with conversion for **1d** only reaching about 4% after 10 d) and for the most sterically encumbered and strongest donor (**1b**) the rearrangement was

halted completely (vide supra). Interestingly, a rate of rearrangement almost equivalent to that observed for **1a** was detected (83% conversion after 5 h) when a bulky phosphine oxide with relatively electron-*withdrawing* phenyl groups (**1e**) was used, and implied that the donor ability of the phosphine oxide has the most significant influence on the rearrangement of [**3**]$^+$ to [**4**]$^+$.

Another significant result came from the reaction between **1e** and **2a**, which appeared to strongly disfavor the formation of [**3h**]$^+$ to the extent that it could not be detected by ^{31}P{^{1}H} NMR which showed only a very slow consumption of starting materials to give [**4**]$^+$, with only 9% conversion in 10 d. This was accelerated when the initial conversion of **1e** and **2a** to [**3h**]$^+$ was increased from being undetectable to 100% by exchange of bromide for triflate, to give 91% conversion in 24 h. This substantial increase in rate of rearrangement, strongly supported the hypothesis that the formation of [**4**]$^+$ was via [**3**]$^+$, with the rate conversion to [**4**]$^+$ strongly dependent on the concentration of [**3**]$^+$.

*(c). Influence of the Silyl Group in **2a** and **5**.* Changing the Me_3Si-substituent on the phosphoranimine **2a** to the more sterically encumbered Ph_3Si group on **5** gave a significant decrease in the rate of the rearrangement, particularly when the bromide counterion was replaced with triflate. The change from **2a** to **5** gave an increase in the time taken for the consumption of [**3**]$^+$ when the anion was Br^- or $[OTf]^-$ of around 10 or 100 times, respectively. These results strongly suggested that the silyl group is intimately involved in the rearrangement reaction, as expected.

(d). Proposed Mechanism. The results obtained and previous studies of somewhat related species[54−56] allowed us to tentatively propose a mechanism for the formation of [**4**]$^+$ after **1** and **2** initially react to form [**3**]$^+$ (Scheme 7). The cation [**3**]$^+$ could undergo an intramolecular rearrangement whereby the phosphoranimine nitrogen nucleophilically attacks the phosphorus center of the ligated phosphine oxide. This could generate an intermediate ([**10**]$^+$, Scheme 7) that is presumably transient and therefore was not observed by NMR. A further rapid rearrangement could then give [**4**]$^+$. Alternative pathways involving the intermediate [**10**]$^+$ might be expected to generate side products that were not structurally characterized. The complex sensitivity of the rate of the rearrangement to the nature of the counteranion could be a consequence of weak coordination at the cationic phosphorus center in [**3**]$^+$ and at the phosphorus or silicon sites in [**10**]$^+$ and the resulting influence on the activation energy for the various reaction steps. The electronic nature of the substituents on the phosphine oxide might be expected to affect the rate of the rearrangement. The observed reduction in rearrangement rate for the electron donating substituents could be due to the lower electrophilicity of the phosphine oxide phosphorus center in [**3**]$^{+}$,[57] possibly making attack by the phosphoranimine nitrogen less favorable. Significantly, $SiMe_3$ groups have a greater established migratory aptitude than their $SiPh_3$ analogues,[42,49,50] and this is consistent with the relative rearrangement rates detected in the cases of the reactions of **1a** with **2a** and **5**.

SUMMARY

A range of phosphine oxides $R_3P{=}O$ (R = ^{t}Me, Et, ^{i}Pr and Ph; **1a**−**e**) have been shown to react with bromophosphoranimines $BrR'R''P{=}NSiMe_3$ (**2**) and $BrMe_2P{=}NSiPh_3$ (**5**) to give a range of O-donor-stabilized phosphoranimine cations ([**3**]$^+$ or [**7**]$^+$). With the exception of those formed by the most sterically encumbered phosphine oxide (**1b**), which permitted the isolation and characterization of the first examples of this new type of stabilized phosphoranimine cation ([**3d**]$^+$ and [**3e**]$^+$), these initial species were found to undergo a rearrangement to the cations [**4**]$^+$ or [**8**]$^+$. A mechanism for this rearrangement was suggested and involves a phosphine migration and silyl group transfer, and is consistent with observed dependencies on the electronic nature of the phosphine oxide and whether the silyl group is -$SiMe_3$ or -$SiPh_3$. No evidence was found in these studies that supported the intermediacy of the cations [**3**]$^+$ or [**4**]$^+$ in the chain growth polycondensation of bromophosphoranimines to form polyphosphazenes.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details (.pdf) and crystallographic information files (.cif). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ian.manners@bristol.ac.uk.

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