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Synthesis, Structures, and Stability of N-Donor-Stabilized N-Silylphosphoranimine Cations

Keith Huynh,[a] Eric Rivard,[a] Alan J. Lough,[a] and Ian Manners*[a, b]

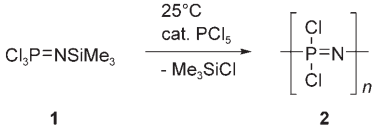
Abstract: A series of DMAP-stabilized (DMAP = 4-dimethylaminopyridine) N-silylphosphoranimine cations $[DMAP{\cdot}PR_2{=}NSiMe_3]^+$, bearing R = Cl ($[\mathbf{8}]^+$), Me ($[\mathbf{10a}]^+$), Me/Ph ($[\mathbf{10b}]^+$), Ph ($[\mathbf{10c}]^+$), and OCH_2CF_3 ($[\mathbf{10d}]^+$) substituents, have been synthesized from the reactions of the parent phosphoranimines $Cl_3P{=}NSiMe_3$ (**3**) and $XR_2P{=}NSiMe_3$ (X = Cl (**9**), Br (**11**); R = Me (**9a** and **11a**), Me/Ph (**9b** and **11b**), Ph (**9c** and **11c**), and OCH_2CF_3 (**9d** and **11d**)) with DMAP and silver salts as halide abstractors. Reactions in the absence of silver salts yield the corresponding cations, with halide counterions. The stability of the salts is highly dependent on the phosphoranimine substituent and the nature of the counteranion, such that electron-withdrawing substituents and non-coordinating anions yield the most stable salts. X-ray structural determination of the cations reveal extremely short phosphoranimine P–N bond lengths for the cations $[\mathbf{8}]^+$ and $[\mathbf{10d}]^+$ (1.47–1.49 Å) in which electron-withdrawing substituents are present and a longer phosphoranimine P–N length for the cation $[\mathbf{10a}]^+$ (1.53 Å) in which electron-donating substituents are present. Very wide bond angles at nitrogen are observed for the salts containing the cation $[\mathbf{10d}]^+$ (158–166°) and indicate significant sp hybridization at the nitrogen centre.

Keywords: cations · donor–acceptor systems · phosphoranimines · polyphosphazenes · substituent effects

Introduction

The study of phosphoranimines with the general formula $R_3P{=}NR'$ (R = alkyl, aryl, or halogen; R′ = alkyl, aryl, or silyl) represents a very rich area of main-group chemistry.[1] Numerous investigations have been carried out in an attempt to further understand the nature of the hypervalent phosphorus(V)–nitrogen double bond and these studies have revealed significant insights into the bonding of phosphoranimines.[2] In addition to a fundamental interest in structure and bonding, phosphoranimines have recently attracted considerable attention due to their application as aza-Wittig reagents,[3] and as ligands in both main-group[4] and transition-metal coordination chemistry.[5] The phosphoranimide ligand $R_3P{=}N^-$, which is derived from N-silylphosphoranimines, has similar steric properties to the ubiquitous cyclopentadienyl ligand and has proven to be an effective ligand for early transition-metal-catalyzed (Ti and Zr) olefin polymerizations.[5b]

In addition to their utilization as ligands, N-silylphosphoranimines are of significant importance as they are also employed as monomeric precursors to polyphosphazenes by means of thermal,[6] fluoride-initiated,[7] and more recently living cationic chain-growth[8] condensation polymerization. Moreover, cationic phosphorus(V)–nitrogen species have been implicated as intermediates in these polymerization mechanisms. For example, the ambient-temperature polymerization of the N-silylphosphoranimine $Cl_3P{=}NSiMe_3$ (**1**), with PCl_5 as a catalyst, yields high-molecular weight polydichlorophosphazene (**2**) (Scheme 1). This process has been shown to proceed via the cationic initiator $[Cl_3P{=}N{=}PCl_3]^+$, $[\mathbf{3}]^+$.[8]



Scheme 1.

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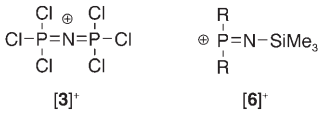
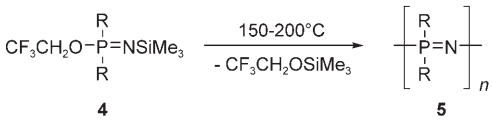


[3]$^+$ [6]$^+$

The thermal (>180 °C) condensation polymerization of a typical phosphoranimine monomer, such as $(CF_3CH_2O)R_2P{=}NSiMe_3$ (**4**) (R = akyl or aryl) yields poly(alkyl/aryl)phosphazenes (**5**) (Scheme 2), yet the mechanism for this process remains unclear. It has been tentatively proposed that the polymerization proceeds through the initial formation of a cationic N-silylphosphoranimine intermediate $[R_2P{=}NSiMe_3]^+$, [**6**]$^+$ from the ionization of the P–O bond in **4**. The cation [**6**]$^+$ might then function as an initiator by inducing the chain-growth polymerization of the remaining N-silylphosphoranimine monomer.[6c]



4 **5**

R = alkyl or aryl

Scheme 2.

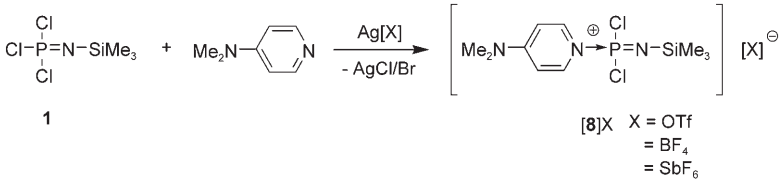
Cations of this type are expected to be extremely Lewis acidic and thus highly reactive due to the coordinatively unsaturated phosphorus(V) centre and would likely require additional stabilization from neutral donors to render them isolable. Indeed, recent studies have shown that employment of nitrogen-based donors has been successful in stabilizing phosphorus cations.[9,10] In this paper, we describe the synthesis and characterization of a series of phosphoranimine cations, which are stabilized by the strong nitrogen-based donor DMAP (4-dimethylaminopyridine). The relative stability of the salts was found to be dependent on both the phosphoranimine substituent and the counteranion.

Results and Discussion

The chemistry of P^{III}–N cations has recently been very well-developed,[9a,11] whereas, in contrast, the study of P^V–N cations with the $[R_2P{=}N{-}R']^+$ framework has been limited to only a few reports over the past two decades. Bertrand, Majoral, and co-workers have reported the generation of iminophosphonium salts, $[(Me_2N)_2P{=}N{-}NMe_2]^+[X]^-$ ($X = PF_6^-$, Br^-), by means of photolysis of an azide-containing phosphonium cation, $[(Me_2N)_3PN_3]^+$. This process has been suggested to proceed through a Curtius-type rearrangement.[12] In addition, Wolf and co-workers have reported the preparation of iminophosphonium salts, $[R_2N{-}P{-}N{=}PR_2]^{2+}$ (R = Me, Et, *i*Pr), from reactions between chlorophosphenium salts, $[R_2N{-}PCl]^+[AlCl_4^-]$, and Me_3SiN_3. Their formation is believed to proceed through a phosphenium azide, $[R_2N{-}P{-}N_3]^+$, intermediate.[13] Finally, Schmutzler and co-workers have reported iminophosphonium salts which are intramolecularly stabilized by a pendant nitrogen donor, $[(NEt_2)((NMe_2)CH_2CH_2N(Me))P{=}N{-}Ph]^+$.[14] While the above examples clearly demonstrate the feasibility of forming phosphorus(V)–nitrogen cations, no structural data has been reported for this novel class of ionic species. Therefore, our aim was to prepare phosphoranimine cations and examine their structure and reactivity. Moreover, investigations into the stability and reactivity of these salts yield further insight into the thermal condensation polymerization mechanism of neutral phosphoranimines.

Reactions of $Cl_3P{=}NSiMe_3$ (1) with Ag salts and DMAP: The stoichiometric reaction between the phosphoranimine $Cl_3P{=}NSiMe_3$ (**1**)[15] and the halide abstractor AgOTf ($OTf = OSO_2CF_3$) was studied. However, in an attempt to generate the triflato derivative $(TfO)Cl_2P{=}NSiMe_3$ (**7**), the quantitative formation of polydichlorophosphazene $[Cl_2P{=}N]_n$ and $TfOSiMe_3$ was observed after 18 hours. The formation of these products was monitored by ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectroscopy. Workup of the resultant polymer by substitution of the P–Cl bonds with $NaOCH_2CF_3$ afforded the polyphosphazene $[(CF_3CH_2O)_2P{=}N]_n$ with molecular weight $M_w = 94{,}000$ and PDI = 1.182 (PDI = polydispersity index). Performing the reaction by using substoichiometric quantities (10–20 mol %) of AgOTf resulted in the incomplete consumption of **1** (approximately 70 %) over a period of two weeks to yield $[Cl_2P{=}N]_n$ and cyclic phosphazene oligomers $[Cl_2P{=}N]_x$, $x = 3$–5. These results suggest that if **7** is indeed initially generated, it immediately oligomerizes due to the labile OTf group at phosphorus.[16]

As pyridine-based ligands have proven successful in the stabilization of cationic phosphorus(III)[9] and, in some cases, phosphorus(V)[9c,d,10] centers, this synthetic strategy was employed in the present system. In the reaction of **1** with a stoichiometric amount of AgOTf and DMAP (DMAP = 4-dimethylaminopyridine), at room temperature over 30 minutes, the clean conversion of **1** ($\delta = -54$ ppm) to a product with a downfield-shifted resonance of $\delta = -40$ ppm in the $^{31}P\{^1H\}$ NMR spectrum was observed (Scheme 3). This product has been isolated and characterized in both solution and

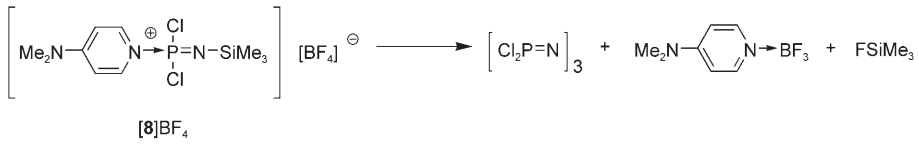


1 [**8**]X X = OTf, BF_4, SbF_6

Scheme 3.

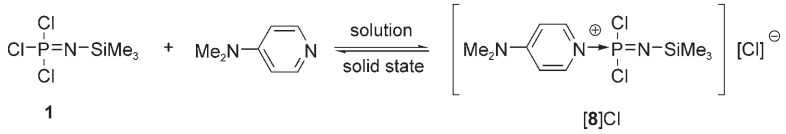
solid-state as a salt containing the novel phosphoranimine cation $[DMAP{\cdot}PCl_2{=}NSiMe_3]^+$, $[\mathbf{8}]^+$.[16]

A variety of analogous salts bearing the cation $[\mathbf{8}]^+$ were also prepared by altering the choice of silver source ($AgBF_4$ and $AgSbF_6$). While the OTf^- and SbF_6^- salts show indefinite stability in both the solution and solid state, $[\mathbf{8}]BF_4$ decomposes over a period of three days to yield the cyclic phosphazene trimer $[Cl_2P{=}N]_3$ ($^{31}P\{^1H\}$ NMR spectroscopy, $\delta = 18$ ppm),[1b] $DMAP{\cdot}BF_3$[17] and volatile Me_3SiF (Scheme 4).



[8]BF4

Scheme 4.

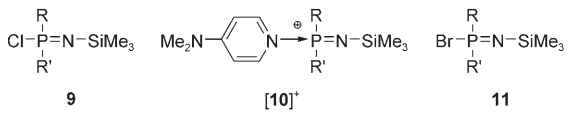


1 [8]Cl

Scheme 5.

Attempts aimed at the generation of cation $[\mathbf{8}]^+$ with Cl^- as the counterion by direct reaction between DMAP and **1**, in the absence of a silver salt, quantitatively yielded [**8**]Cl. Remarkably, in the solid state, this species slowly reconverts back to **1** and free DMAP over a period of two weeks at ambient temperature, but this reaction can be reversed upon redissolution in CH_2Cl_2. This phenomenon indicated the presence of an equilibrium between the product and the reagents. The equilibrium was manipulated in solution with the sequential addition of 0.25 molar equivalents of $[Ph_3P{=}N{=}PPh_3]Cl$, which results in the complete retroconversion of [**8**]Cl to **1** and free DMAP after the addition of one equivalent of chloride ion (Scheme 5).[16]

The above results show that the stability of $[\mathbf{8}]^+$ depends critically on the nature of the counterion. It is initially evident that the cation $[\mathbf{8}]^+$ is most stable when coupled with inert, weakly coordinating anions, such as OTf^- and SbF_6^-, whereas more reactive or more strongly coordinating anions such as BF_4^- and Cl^- yield decomposition products. Therefore, the preparation of various analogues of $[\mathbf{8}]^+$, with different substituents at phosphorus, was explored in an attempt to better understand the factors which govern the stability of this new class of phosphoranimine cation.

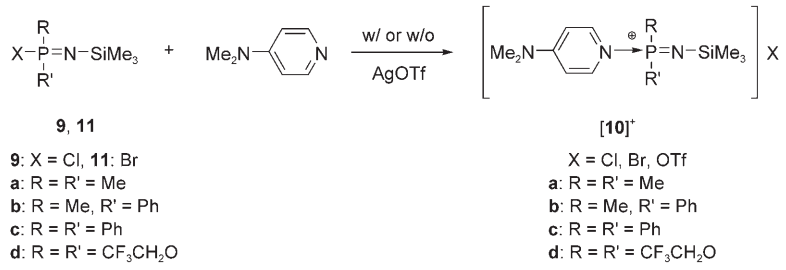


9 [10]+ 11

a: R = R' = Me
b: R = Me, R' = Ph
c: R = R' = Ph
d: R = R' = OCH_2CF_3

Reactions of $ClMe_2P{=}NSiMe_3$ (9a) and $BrMe_2P{=}NSiMe_3$ (11a) with DMAP in the presence or absence of AgOTf: The cation $[\mathbf{8}]^+$ bears electron-withdrawing chlorine substituents. Our next target was to prepare an analogous species with electron-donating substituents, such as methyl, in an effort to probe the relative stability of the phosphoranimine cations with respect to the substituents at phosphorus. In an analogous reaction between DMAP and the phosphoranimine $ClMe_2P{=}NSiMe_3$ (**9a**),[18] in the presence of AgOTf, the immediate precipitation of a white solid (AgCl) was observed. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture after two hours showed the exclusive formation of the desired cation with a downfield-shifted resonance of $\delta = 26$ ppm for $[\mathbf{10a}]^+$ from that of the precursor at $\delta = 24$ ppm (**9a**). The reaction between **9a** and DMAP without AgOTf yielded the same cation but with Cl^- as the counteranion, [**10a**]Cl. However, upon the dissolving single crystals of [**10a**]Cl only partial retroconversion to the parent phosphoranimine $ClMe_2P{=}NSiMe_3$ (**9a**) (30%) and free DMAP was detected by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Intrigued by this result, the same cation with a different halide as the counteranion was prepared. Treatment of the phosphoranimine $BrMe_2P{=}NSiMe_3$ (**11a**)[19] ($^{31}P\{^1H\}$ NMR spectroscopy, $\delta = 10$ ppm) with a stoichiometric quantity of DMAP yielded the salt $[DMAP{\cdot}PMe_2{=}NSiMe_3]Br$, [**10a**]Br, as characterized by NMR spectroscopy and single-crystal X-ray diffraction. Surprisingly, no retroconversion of [**10a**]Br to the parent phosphoranimine **11a** was detected when crystals of [**10a**]Br were dissolved in $CHCl_3$. These results indicate that while the dimethyl-substituted cation $[\mathbf{10a}]^+$ is more stable towards retroconversion than the analogous system with chlorine substituents $[\mathbf{8}]^+$, the stability of $[\mathbf{10a}]^+$ is still dependent on the identity of the counteranion (Scheme 6).

Reactions of $ClMePhP{=}NSiMe_3$ (9b), $BrMePhP{=}NSiMe_3$ (11b), and $ClPh_2P{=}NSiMe_3$ (9c) with DMAP in the presence or absence of AgOTf: In a parallel reaction between $ClMePhP{=}NSiMe_3$ (**9b**)[20] and DMAP, in the presence of AgOTf, the expected salt $[DMAP{\cdot}PMePh{=}NSiMe_3]OTf$, [**10b**]OTf, was obtained in quantitative yield. However in the absence of AgOTf, an incomplete reaction between $ClMePhP{=}NSiMe_3$ and DMAP was observed. The $^{31}P\{^1H\}$ and ^1H NMR spectra of the reaction between **9b** and DMAP in $CDCl_3$ were analyzed after 1 h and revealed only 12% conversion of **9b** ($^{31}P\{^1H\}$ NMR spectroscopy, $\delta =$



Scheme 6.

16 ppm) to the desired salt [DMAP·PMePh=$NSiMe_3$]Cl, [**10b**]Cl, ($^{31}P\{^1H\}$ NMR spectroscopy, $\delta = 17$ ppm). No changes were observed in the NMR spectra after stirring for two days. In contrast when the phosphoranimine BrMePhP=$NSiMe_3$ (**11b**)[19] was treated with DMAP, the full conversion of **11b** ($^{31}P\{^1H\}$ NMR spectroscopy, $\delta = 4$ ppm) to the salt [DMAP·PMePh=$NSiMe_3$]Br, [**10b**]Br, ($^{31}P\{^1H\}$ NMR spectroscopy, $\delta = 17$ ppm) was observed after one hour.

As the reaction between **9b** and DMAP resulted in an incomplete reaction, we were interested to determine if the phosphoranimine $ClPh_2P{=}NSiMe_3$ (**9c**)[18] would behave in a similar manner. When $ClPh_2P{=}NSiMe_3$ (**9c**) was treated with a stoichiometric amount of DMAP in $CDCl_3$, an incomplete (37%) conversion of **9c** ($^{31}P\{^1H\}$ NMR spectroscopy, $\delta = 9$ ppm) to the desired salt [DMAP·PPh_2=$NSiMe_3$]Cl, [**10c**]Cl, ($^{31}P\{^1H\}$ NMR spectroscopy, $\delta = 12$ ppm) was observed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Similar to **9b**, no further detectable change in the composition of the reaction mixture was observed after two days. However in the presence of AgOTf, the quantitative conversion of **9c** to the salt [DMAP·PPh_2=$NSiMe_3$]OTf, [**10c**]OTf, was observed and the latter was characterized by multinuclear NMR spectroscopy. As the phosphoranimine $BrPh_2P{=}NSiMe_3$ (**11c**) cannot be prepared due to decomposition during purification,[18] the reaction between **11c** and DMAP was not attempted.

Reactions of $Cl(CF_3CH_2O)_2P{=}NSiMe_3$ (9d) and $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (11d) with DMAP in the presence or absence of silver salts: As alkyl and aryl substituents appear to destabilize the cationic phosphorus centre in the presence of Cl^- as the counteranion, we used the more electronegative CF_3CH_2O[21] substituent to stabilize the cation. Similar treatment of $Cl(CF_3CH_2O)_2P{=}NSiMe_3$ (**9d**) ($^{31}P\{^1H\}$ NMR spectroscopy, $\delta = -16$ ppm), prepared in situ, with DMAP and AgOTf resulted in the quantitative formation of a new product with a $^{31}P\{^1H\}$ NMR spectroscopic shift of $\delta = -22$ ppm (Scheme 6). The resultant species was isolated as a white solid and characterized in both solution and in the solid state as the new phosphoranimine salt [DMAP·$P(OCH_2CF_3)_2$=$NSiMe_3$]OTf, [**10d**]OTf.

In the absence of AgOTf, the reaction between **9d**, prepared in situ, with DMAP also yielded the cation [**10d**]$^+$ with the anticipation of Cl^- as the counteranion. Surprisingly, upon isolation and recrystallization of the crude material, analysis of the resulting crystals by X-ray diffraction (see next section) revealed $SO_2{\cdot}Cl^-$ as the counteranion instead of Cl^-, [**10d**]Cl·SO_2. The coordination of the chloride counteranion to SO_2 likely resulted from dissolved SO_2 byproduct in the preparation of **9d**. Interestingly, upon dissolution of single crystals of [**10d**]Cl·SO_2 in $CDCl_3$, the partial dissociation of DMAP from the phosphorus centre in [**10d**]$^+$ was observed, which yielded **9d** and DMAP·SO_2 (**12**) as indicated by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The presence of **12** was confirmed when the resultant NMR sample was recrystallized and single crystals were examined by X-ray diffraction.[22] The DMAP·SO_2 adduct was also independently synthesized by bubbling SO_2 gas through a CH_2Cl_2 solution of DMAP for 15 minutes.[23] Workup and recrystallization from CH_2Cl_2 yielded **12** as clear colorless crystals.

Not surprisingly, when reaction between the phosphoranimine $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**11d**)[19] and DMAP in the absence of a silver salt was investigated, the quantitative formation of the stable salt [DMAP·$P(OCH_2CF_3)_2$=$NSiMe_3$]Br, [**10d**]Br, was observed. This compound is indefinitely stable in both the solution and solid state and was also structurally characterized by a single-crystal X-ray diffraction study.[22] Encouraged by the substantial increase in stability for the cation [**10d**]$^+$ compared to [**8**]$^+$ and [**10c**]$^+$, **11d** was treated with DMAP in the presence of $AgBF_4$, in an effort to prepare [**10d**]BF_4, and examine the possibility of its decomposition to the cyclic trimer $[(CF_3CH_2O)_2P{=}N]_3$, DMAP·BF_3 and Me_3SiF, as was observed for [**8**]BF_4 (Scheme 4). Surprisingly, upon workup and recrystallization, [**10d**]BF_4 was obtained in high yield. Crystals of [**10d**]BF_4 are indefinitely stable in solution and its solid-state structure was confirmed by a single-crystal X-ray diffraction study.

Structural characterization of DMAP-stabilized phosphoranimine cations by X-ray diffraction: Views of the formula units for [**8**]OTf, [**10a**]Br, [**10d**]OTf, [**10d**]Cl·SO_2, [**10d**]Br, and [**10d**]BF_4 determined by X-ray diffraction (Table 1) are shown in Figures 1–6. Selected bond lengths and angles for the phosphoranimine salts are given in Table 2. The P(1)–N(3) bond lengths for the cations [**8**]$^+$ and [**10a**,**d**]$^+$ range from 1.490(3) to 1.526(2) Å (Table 2) and are shorter than typical phosphorus–nitrogen double-bond lengths which range from 1.54 to 1.58 Å.[24] In particular, the phosphoranimine bond distances of 1.490(3) and 1.486(2) Å, found in [**8**]$^+$ and [**10d**]$^+$ respectively, approach the observed 1.475(8) Å bond length found in the iminophosphonium cation [P≡NMes*]$^+$, [**13**]$^+$, (Mes* = 2,4,6-tri-*tert*-butylphenyl) in which a formal triple bond exists between phosphorus(III) and nitrogen.[11a] These bond distances are among some of the shortest observed between phosphorus(V) and nitrogen. To the best of our knowledge, the shortest P^V–N distance is

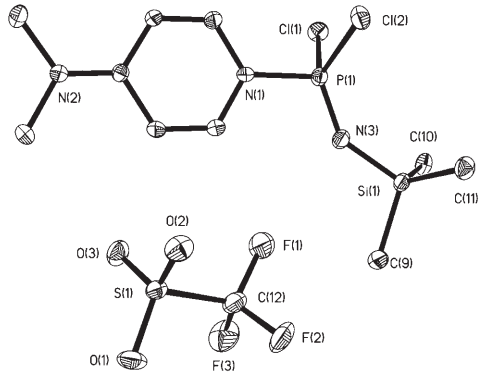


Figure 1. Thermal ellipsoid of [**8**]OTf at the 50% probability level. All hydrogen atoms are omitted for clarity.

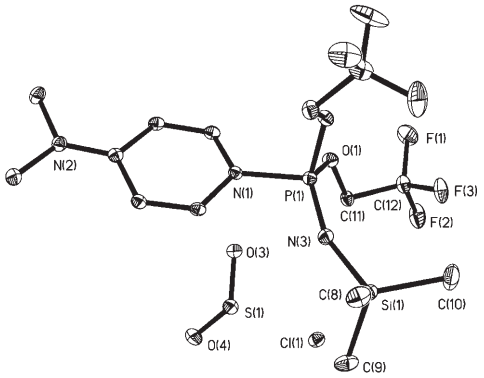


Figure 4. Thermal ellipsoid plot of [**10d**]Cl·SO_2 at the 50% probability level. All hydrogen atoms are omitted for clarity.

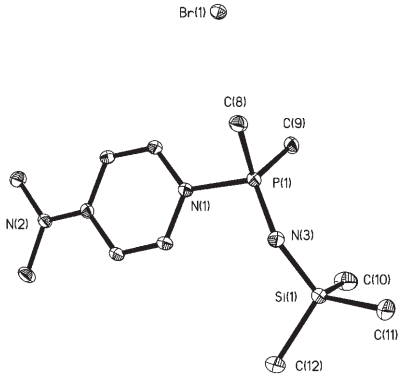


Figure 2. Thermal ellipsoid plot of [**10a**]Br at the 50% probability level. All hydrogen atoms are omitted for clarity.

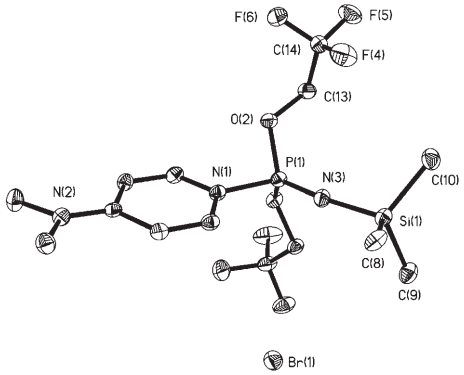


Figure 5. Thermal ellipsoid plot of [**10d**]Br at the 50% probability level. All hydrogen atoms are omitted for clarity.

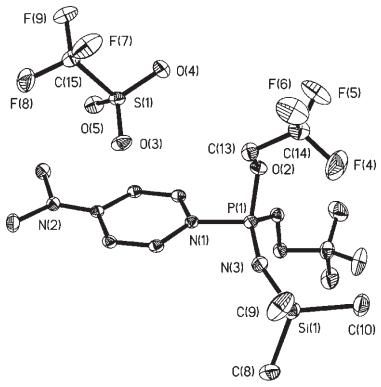


Figure 3. Thermal ellipsoid plot of [**10d**]OTf at the 50% probability level. All hydrogen atoms are omitted for clarity.

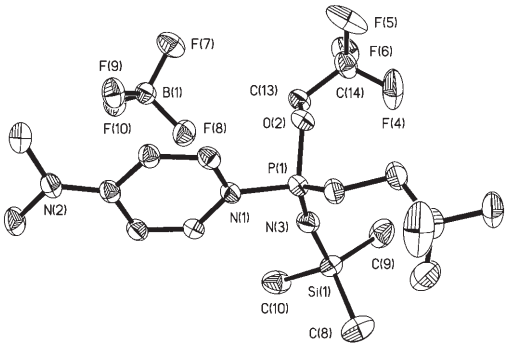


Figure 6. Thermal ellipsoid plot of [**10d**]BF_4 at the 50% probability level. All hydrogen atoms are omitted for clarity.

currently found in the phosphoranimine $Cl_3P{=}NMes^*$ (**14a**),[25] which exhibits a P–N bond length of 1.467(4) Å.

The internal phosphoranimine nitrogen bond angles, P-N-Si, found in the cations [**8**]$^+$ and [**10a**,**d**]$^+$ are large and range from 141.74(13)–166.7(2)° (Table 2). The nitrogen bond angle of 166.7(2)° found in [**10d**]Br approaches the P-N-C angle of 177.0(7)° found in [**13**]$^+$ in which a formally sp-hybridized nitrogen centre is present. The short P–N bond lengths and large nitrogen bond angles found in the phosphoranimine cations [**8**]$^+$, [**10a**]$^+$, and [**10d**]$^+$ suggests a significant degree of electron delocalization from the phosphoranimine nitrogen lone pair into the P–N bond and thus involve considerable sp hybridization at the nitrogen

$P{\equiv}N{-}Mes^*$ [**13**]$^+$ | $Cl_3P{=}N{-}Mes^*$ **14a** | $Cl_3P{\equiv}N{-}Mes^*$ **14b** | $N{\rightarrow}P{\equiv}N{-}Mes^*$ [**15**]$^+$

Table 1. Crystal data for [**8**]OTf, [**10a**]Br, [**10d**]OTf, [**10d**]Cl·SO_2, [**10d**]Br, and [**10d**]BF_4.

	[**8**]OTf	[**10a**]Br	[**10d**]OTf	[**10d**]Cl·SO_2	[**10d**]Br	[**10d**]BF_4
empirical formula	$C_{11}H_{19}Cl_2F_3N_3O_3PSSi$	$C_{12}H_{25}BrN_3PSi$	$C_{15}H_{23}F_9N_3O_5PSSi$	$C_{14}H_{23}ClF_6N_3O_4PSSi$	$C_{14}H_{23}BrF_6N_3O_2PSi$	$C_{14}H_{13}BF_{10}N_3O_2PSi$
F_w	460.31	350.32	587.48	537.92	518.32	525.22
crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a [Å]	8.0840(4)	7.2268(2)	9.2974(3)	9.5083(6)	12.8002(6)	19.7587(9)
b [Å]	8.6430(4)	10.0545(3)	10.6398(3)	9.8829(5)	12.6209(5)	8.1806(6)
c [Å]	14.6080(7)	12.3741(4)	12.7808(4)	12.8928(10)	13.2910(6)	14.9525(16)
α [°]	88.5630(19)	85.0680(18)	92.746(2)	94.181(4)	90	90
β [°]	86.5950(18)	87.268(2)	94.4460(15)	104.059(3)	91.250(3)	98.091(5)
γ [°]	85.038(2)	74.3610(18)	93.973(3)	90.481(4)	90	90
V [Å^3]	1014.84(8)	862.35(4)	1255.67(7)	1171.69(13)	2146.65(16)	2394.4(3)
Z	2	2	2	2	4	4
ρ_{calcd} [mg m^{-3}]	1.506	1.349	1.554	1.525	1.604	1.457
T [K]	150(1)	150(1)	150(1)	150(1)	150(2)	150(1)
R ($I>2\sigma(I)$)	0.0550	0.0342	0.0438	0.0483	0.0477	0.0565
wR ($I>2\sigma(I)$)	0.1513	0.0893	0.1197	0.1338	0.1304	0.1689
Gof on F^2	0.987	1.046	1.032	1.025	1.018	1.014

Table 2. Selected bond lengths and angles for $[\mathbf{8}]^+$, $[\mathbf{10a}]^+$, $[\mathbf{10d}]^+$, and related compounds.

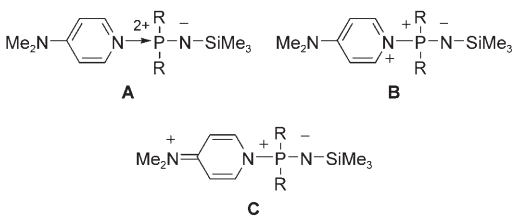
	P(1)–N(3) [Å]	P(1)–N(1) [Å]	P(1)-N(3)-E [°]
[**8**]OTf	1.490(3)	1.713(2)	144.1(2) (E = Si)
[**10a**]Br	1.526(2)	1.7946(19)	141.74(13) (E = Si)
[**10d**]OTf	1.4894(18)	1.7278(18)	159.63(15) (E = Si)
[**10d**]Cl·SO_2	1.486(2)	1.731(2)	158.48(17) (E = Si)
[**10d**]Br	1.476(3)	1.724(3)	166.7(2) (E = Si)
[**10d**]BF_4	1.489(3)	1.711(3)	166.1(3) (E = Si)
[**13**]$AlCl_4$[11a]	1.475(8)	N/A	177.0(7) (E = C)
14[25]	1.4674(4)	N/A	160.9(3) (E = C)
[**15**]OTf[11b]	1.472(8)	1.958(8)	161.7(7) (E = C)

centre. In addition, it has been speculated that the short P–N bond length and wide nitrogen bond angle (160.9(3)°) found in **14a** results from the steric imposition created on the phosphoranimine moiety by the Mes* substituent. This constraint results in the possible zwitterionic resonance form **14b** which is believed to be a major contributor to the solid-state structure.[25]

The DMAP ligand is strongly bound to the phosphorus centre in the cations $[\mathbf{8}]^+$ and $[\mathbf{10a,d}]^+$ with N(1)–P(1) bond distances between 1.711(3) and 1.7964(19) Å, which are shorter than that observed for $[\mathbf{15}]^+$ (1.958(8) Å),[11b] in which pyridine is the donor. It is noteworthy the DMAP–P bond distances are significantly shorter (1.713(2)–1.731(2) Å) for the phosphoranimine cations $[\mathbf{8}]^+$ and $[\mathbf{10d}]^+$, in which electron-withdrawing substituents (Cl and OCH_2CF_3) are present, compared to $[\mathbf{10a}]^+$ in which the electron-donating Me substituent is present (1.7946(19) Å). The shorter DMAP–P distance observed for $[\mathbf{8}]^+$ and $[\mathbf{10d}]^+$ deviates significantly from the idealized phosphorus–nitrogen single bond length of 1.800(4) Å.[26]

It is clear that the key structural features of the cations $[\mathbf{8}]^+$ and $[\mathbf{10a,d}]^+$ are highly dependent on the substituents at phosphorus. Specifically, the presence of a highly electron-withdrawing substituent, such as CF_3CH_2O, yield cations with extremely short phosphoranimine P^V–N bonds, wide internal phosphoranimine nitrogen bond angles, and shortened DMAP–P^V bonds. In contrast, the presence of electron-donating substituents, such as Me, yield cations with longer phosphoranimine P^V–N bonds, narrow internal phosphoranimine nitrogen bond angles and lengthened DMAP–P^V bonds.

Discussion on bonding and reactivity: While the donor-stabilized phosphoranimine cations $[\mathbf{8}]^+$ and $[\mathbf{10}]^+$ have been represented as species containing formal P–N double bonds, alternative bonding models are available. The valence-bond description of the unsaturated phosphorus(V)–nitrogen bond requires hypervalency at the phosphorus centre and thus, d-orbital participation must be invoked for $d\pi_P$–$p\pi_N$ overlap to occur in order to achieve the formal π bond.[2a,b] Recent ab initio investigations have shown that d orbitals usually have an insignificant contribution to bonding amongst the main-group elements[2c,d] due to their high energy, and an ionic-bonding model is more suitable in describing the P^V–N bond. Phosphoranimines, like phosphorus ylides, can be represented by a zwitterionic structure with a polarized single bond.[27,28] This bonding depiction would account for the short phosphorus–nitrogen bond lengths observed in phosphoranimines. By using this bonding model, three structures are possible in the description of bonding in the donor-stabilized phosphoranimine cations. A dicationic charge may be placed on the phosphorus centre (**A**), two positive charges may be placed adjacent to each other (**B**) or a positive charge may be delocalized onto the dimethylamino functionality of the ligand (**C**).



While this description accounts for the short P–N bonds observed in the cations $[\mathbf{8}]^+$ and $[\mathbf{10}]^+$, it does not account for the observed wide nitrogen bond angles, particularly in $[\mathbf{10d}]^+$. Negative hyperconjugation[29] is an additional alternative and a more appropriate model for the bonding description of $[\mathbf{8}]^+$ and $[\mathbf{10}]^+$. 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.[2e] Thus, the employment of extremely electronegative substituents, such as CF_3CH_2O, effectively lowers the energy of the σ^*_{PR} orbitals and therefore allows more efficient π_N–σ^*_{PR} overlap. The improved π_N–σ^*_{PR} interaction for electronegative substituents thus results in the extremely wide nitrogen bond angle observed in $[\mathbf{10d}]^+$. Moreover, the narrowed nitrogen bond angle (141.74(13)°) observed in $[\mathbf{10a}]^+$ is a result of less efficient π_N–σ^*_{PR} overlap due the electron-donating methyl group.

The cations $[\mathbf{8}]^+$ and $[\mathbf{10}]^+$ represent donor-stabilized surrogates of $[\mathbf{6}]^+$ and are illustrative model complexes for the reactive intermediate in the proposed thermal condensation polymerization mechanism of phosphoranimines (**4**). Consequently, the catalytic activity of these cations was tested toward polymerization of the neutral phosphoranimines. However, in substoichiometric reactions between DMAP (10 mol%) and the phosphoranimines $Cl_3P{=}NSiMe_3$ (**1**), $BrMe_2P{=}NSiMe_3$ (**11a**), $BrMePhP{=}SiMe_3$ (**11b**), and $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**11d**) no polymerization was detected. Instead, the quantitative formation of the respective donor-stabilized cation ([**8**]Cl, [**10a**]Br, [**10b**]Br, or [**10d**]Br) was observed and the residual phosphoranimine remained unreacted. These reactions indicate that the DMAP ligand is tightly bound to the phosphorus centre, and thereby inhibits the propagation step of polymerization. This property could potentially be averted and allow for polymerization to proceed at ambient or lower temperatures by the employment of weaker phosphorus-based donors, such as phosphines[30,31] R_3P and phosphites[31] $(RO)_3P$. Studies in this direction, in addition to further mechanistic investigations on the thermal condensation polymerization of phosphoranimines are currently underway.

Conclusions

A series of cationic phosphoranimines bearing chloro, methyl, phenyl, and trifluoroethoxy substituents, which are stabilized by the strong nitrogen-based donor DMAP, have been prepared. These cations exhibit varied stability depending on the substituent system and the counteranion. The chloride salts of these cations yield unstable compounds in that they readily recombine to form the parent phosphoranimines and free DMAP. Structural analysis of the cations indicate substantial multiple-bond character for the phosphorus(V)–nitrogen phosphoranimine bond from their short bond lengths and their obtuse nitrogen bond angles. The shortest phosphoranimine P–N bonds, and the widest internal nitrogen bond angles were observed for the cations bearing electronegative substituents at phosphorus. In contrast, electron-releasing substituents, such as Me, result in cations with lengthened P^V–N bonds and narrowed bond angles at nitrogen, and these structural features have been rationalized by using the negative hyperconjugation model. As a result of the increased donor-stabilization, these cations exhibit no catalytic activity toward the polymerization of their parent phosphoranimines and investigations toward employment of weaker bases, with the anticipation of increased reactivity toward polymerization, are currently in progress.[30,31]

Experimental Section

General: All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen or argon (BOC Gases) by using common Schlenk techniques or an inert atmosphere glove box (M-Braun). Hexanes were dried and collected by using a Grubbs-type solvent purification system manufactured by M-Braun.[32] CH_2Cl_2 and $CHCl_3$ were dried at reflux over CaH_2. Et_2O was dried at reflux over Na/benzophenone. ^1H, $^{13}C\{^1H\}$, ^{19}F, ^{11}B, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian Gemini 300 spectrometer (300.1, 75.4, 282.3, 96.3, and 121.5 MHz) and were referenced either to protic impurities in the solvent (^1H) or externally to $SiMe_4$ ($^{13}C\{^1H\}$ NMR), $CFCl_3$ (^{19}F NMR) in $CDCl_3$, $BF_3{\cdot}Et_2O$ (^{11}B NMR), and 85% H_3PO_4 ($^{31}P\{^1H\}$ NMR) in $CDCl_3$. Mass spectra were obtained with the use of a VG-250S mass spectrometer by using a 70 eV electron impact ionization source. Elemental analyses were performed at the University of Toronto by using a Perkin–Elmer 2400 Series CHN Analyzer. Sulfuryl chloride (SO_2Cl_2) was distilled under nitrogen prior to use. 4-Dimethylaminopyridine (DMAP) and $[Ph_3PNPPh_3]Cl$ were purchased from Aldrich and used as received. The silver salts AgOTf, $AgBF_4$, and $AgSbF_6$ were also purchased from Aldrich and were dried under dynamic vacuum at 100°C, in the absence of light, for 24 h prior to use. $Cl_3P{=}NSiMe_3$ (**1**),[15] $ClMe_2P{=}NSiMe_3$ (**9a**),[18] $ClMePhP{=}NSiMe_3$ (**9b**),[20] $ClPh_2P{=}NSiMe_3$ (**9c**),[18] $BrMe_2P{=}NSiMe_3$ (**11a**),[19] $BrMePhP{=}NSiMe_3$ (**11b**),[19] and $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**11d**)[19] were prepared according to literature procedures.

X-ray structure determination: Data were collected on a Nonius Kappa-CCD diffractometer by using graphite-monochromated $Mo_{K\alpha}$ 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 by using the Denzo-SMN package.[33] The structures were solved and refined with the SHELXTL-PC v6.12 software package.[34] Refinement was by full-matrix least-squares on F^2 by using data (including negative intensities) with hydrogen atoms bonded to carbon atoms included in calculated positions and treated as riding atoms. CCDC-233426, 623882–623887 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

Reaction between $Cl_3P{=}NSiMe_3$ (1) and AgOTf: A CH_2Cl_2 (5 mL) solution of **1** (1.56 g, 6.95 mmol) was rapidly added to a CH_2Cl_2 suspension of AgOTf (1.79 g, 6.97 mmol) in the absence of light. The resulting white suspension was stirred for 18 h and then filtered and reduced to dryness. The residue was redissolved in Et_2O (50 mL) then cooled to 0°C and treated with a freshly prepared solution of $NaOCH_2CF_3$ (100 mL, 16.5 M/THF). Upon complete addition, the resulting suspension was allowed to warm to ambient temperature and then refluxed for 6 h. Filtration of the white suspension yielded a clear and colorless filtrate. The solvent was removed in vacuo and afforded a white solid. The crude polymer was redissolved in THF (3 mL) and purified by successive precipitations into water and then hexanes which resulted in pure $[(CF_3CH_2O)_2P{=}N]_n$ (0.93 g, 55%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -7.3$ ppm (s); ^1H NMR ($CDCl_3$): $\delta = 4.6$ ppm (br); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 63.7$ (OCH_2CF_3),

121.7 ppm (q, $^1J_{C,F}=321.1$ Hz; OCH_2CF_3); ^{19}F NMR ($CDCl_3$): $\delta=-75.0$ ppm; GPC: $M_w=94{,}000$ gmol^{-1}; $M_n=79{,}600$ gmol^{-1}; PDI = 1.182.

[DMAP·PCl$_2$=NSiMe$_3$]OTf [8]OTf: In the absence of light, a CH_2Cl_2 (3 mL) solution of $Cl_3P{=}NSiMe_3$ (**1**) (1.94 g, 8.63 mmol) was added dropwise to a stirring CH_2Cl_2 suspension of DMAP (1.06 g, 8.67 mmol) and AgOTf (2.21 g, 8.63 mmol) at ambient temperature. The resulting white suspension was stirred for 30 min followed by filtration. Slow evaporation of the filtrate yielded large colorless needles of [**8**]OTf (3.26 g, 82%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=-39.8$ ppm; ^1H NMR ($CDCl_3$): $\delta=0.30$ (s, 9H; $SiMe_3$); 3.51 (s, 6H; NMe_2), 7.31 (dd, $J=2.7$, 8.4 Hz, 2H; *m*-H, DMAP), 8.46 ppm (dd, $J=7.4$, 10.7 Hz, 2H; *o*-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta=1.7$ (d, $^3J_{C,P}=5.0$ Hz; $SiMe_3$), 41.5 (s; NMe_2), 108.9 (d, $^3J_{C,P}=8.0$ Hz; *m*-C, DMAP), 120.5 (q, $^1J_{C,F}=166.1$ Hz; OTf), 138.7 (d, $^2J_{C,P}=5.0$ Hz; *o*-C, DMAP), 157.8 ppm (s; *p*-C, DMAP); ^{19}F NMR ($CDCl_3$): $\delta=-78.2$ ppm (s; OTf); EIMS (70 eV): *m*/*z* (%): 312 (2) $[M-OTf]^+$, 208 (1) $[Cl_3P{=}NSiMe_3{-}Me]^+$, 189 (4) $[Cl_2P{=}NSiMe_3]^+$, 155 (8) $[ClP{=}NSiMe_3]^+$, 121 (100) $[DMAP]^+$, 69 (64) $[CF_3]^+$; elemental analysis calcd (%) for $C_{11}H_{19}N_3Cl_2O_3PSSi$ (460.3): C 28.70, H 4.16, N 9.13; found: C 28.50, H 3.98, N 9.05.

[DMAP·PCl$_2$=NSiMe$_3$]BF$_4$ [8]BF$_4$: In the absence of light, a solution of **1** (0.28 g, 0.12 mmol) in CH_2Cl_2 (1 mL) was added to a mixture of DMAP (0.15 g, 0.12 mmol) and $AgBF_4$ (0.25 g, 0.13 mmol) in CH_2Cl_2 (2 mL). The reaction was stirred for 30 min to give a white suspension. The AgCl was filtered off and the volatiles were removed from the filtrate to give a white solid (0.31 g, 62%) which was identified as [**8**]BF_4 by NMR spectroscopy. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=-39.8$ ppm (s); ^1H NMR ($CDCl_3$): $\delta=0.25$ (s, 9H; $SiMe_3$), 3.44 (s, 6H; NMe_2), 7.20 (br s, 2H; *m*-H, DMAP), 8.40 ppm (br s, 2H; *o*-H, DMAP); ^{19}F NMR ($CDCl_3$): $\delta=-151.4$ ppm (pseudo q; BF_4^-).

Compound [**8**]BF_4 gradually decomposed over a period of 3 d in $CDCl_3$ to give $[Cl_2P{=}N]_3$ and DMAP·BF_3.

Data for decomposition products: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=20.0$ ppm (s; $[Cl_2P{=}N]_3$); ^1H NMR ($CDCl_3$): $\delta=3.20$ (s, 6H; NMe_2), 6.66 (d, $J=7.0$ Hz, 2H; *m*-H), 8.10 ppm (br s, 2H; *o*-H); ^{19}F NMR ($CDCl_3$): $\delta=-151.6$ ppm (m); ^{11}B NMR ($CDCl_3$): $\delta=-0.02$ ppm (br).

Literature data for DMAP·BF_3:[17] ^1H NMR ($CDCl_3$): $\delta=3.16$ (s), 6.61 (d, $J=7.0$ Hz), 8.09 ppm (br); ^{19}F NMR ($CDCl_3$): $\delta=-152.7$ ppm (m); ^{11}B NMR ($CDCl_3$): $\delta=0.34$ ppm (br).

[DMAP·PCl$_2$=NSiMe$_3$]SbF$_6$ [8]SbF$_6$: In the absence of light, a solution of **1** (90 mg, 0.40 mmol) in $CDCl_3$ (0.5 mL) was added quickly to a stirred mixture of $AgSbF_6$ (138 mg, 0.40 mmol) and DMAP (49 mg, 0.40 mmol) in $CDCl_3$ (1 mL). The resulting grey suspension was stirred for 30 min and the AgCl was filtered off. Analysis of the resulting colorless filtrate by NMR spectroscopy indicated the formation of [**8**]SbF_6 (95% pure; trace of unreacted **1**, $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=-54.0$ ppm (s), was present). Compound [**8**]SbF_6 was stable in solution for up to two weeks without any noticeable sign of decomposition. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=-40.2$ ppm (s); ^1H NMR ($CDCl_3$): $\delta=0.24$ (s, 9H; $SiMe_3$), 3.38 (s, 6H; NMe_2), 7.04 (dd, $J=3.2$, 7.1 Hz, 2H; *m*-H, DMAP), 8.34 ppm (dd, $J=8.1$, 11.1 Hz, 2H; *o*-H, DMAP); ^{19}F NMR ($CDCl_3$): $\delta=-110$ (very br), -135 ppm (very br; SbF_6^-).

[DMAP·PCl$_2$=NSiMe$_3$]Cl [8]Cl: A solution of DMAP (47 mg, 0.38 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to a solution of $Cl_3P{=}NSiMe_3$ (**1**) (93 mg, 0.41 mmol) in CH_2Cl_2 (1 mL). The resulting colorless solution was stirred for 1 h and the volatiles (including any excess $Cl_3P{=}NSiMe_3$) were removed in vacuo to give a white solid (110 mg, 82%); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=-39.2$ ppm (s); ^1H NMR ($CDCl_3$): $\delta=0.08$ (s, 9H; $SiMe_3$), 3.46 (s, 6H; NMe_2), 7.65 (dd, $J=3.0$, 8.1 Hz, 2H; *m*-H, DMAP), 8.37 ppm (dd, $J=8.4$, 10.1 Hz, 2H; *o*-H, DMAP); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta=1.7$ (d, $^3J_{C,P}=4.5$ Hz; $SiMe_3$), 42.1 (s; NMe_2), 109.7 (d, $^3J_{C,P}=8.6$ Hz; *m*-C, DMAP), 138.6 (d, $^2J_{C,P}=5.9$ Hz; *o*-C, DMAP), 157.8 ppm (s; *p*-C, DMAP). To investigate the equilibrium nature of [**8**]Cl, sequential amounts of chloride ion, as $[Ph_3P{=}N{=}PPh_3]Cl$, was added to a freshly prepared solution of [**8**]Cl in $CDCl_3$.

[DMAP·PMe$_2$=NSiMe$_3$]OTf [10a]OTf: To a stirring $CHCl_3$ suspension of DMAP (0.21 g, 1.73 mmol) and AgOTf (0.44 g, 1.73 mmol) was added a $CHCl_3$ solution of either $ClMe_2P{=}NSiMe_3$ (**9a**) or $BrMe_2P{=}NSiMe_3$ (**11a**) (1.73 mmol). The white suspension was stirred for 2 h followed by filtration of the silver halide. The filtrate was reduced to dryness and the resulting white crystalline solid recrystallized by Et_2O vapor diffusion onto a saturated $CHCl_3$ solution of [**10a**]OTf (0.52 g, 72%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=26.2$ ppm (s); ^1H NMR ($CDCl_3$): $\delta=0.00$ (s, 9H; $SiMe_3$), 1.90 (d, $^2J_{H,P}=13.8$ Hz, 6H; P–Me), 3.23 (s, 6H; NMe_2), 6.90 (d, $J=7.8$ Hz, 2H; *m*-H, DMAP), 8.47 ppm (t, $J=7.2$ Hz, 2H; *o*-H, DMAP); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta=3.3$ (s; $SiMe_3$), 19.8 (d, $^1J_{C,P}=81.3$ Hz; P–Me), 40.5 (s; NMe_2), 108.1 (d, $^3J_{C,P}=4.6$ Hz; *m*-C, DMAP), 120.8 (q, $^1J_{C,F}=320.5$ Hz; OTf), 139.8 (d, $^2J_{C,P}=5.3$ Hz; *o*-C, DMAP), 157.4 ppm (s; *p*-C, DMAP); ^{19}F NMR ($CDCl_3$): $\delta=-78.2$ ppm (s; OTf).

[DMAP·PMe$_2$=NSiMe$_3$]Cl [10a]Cl: A $CHCl_3$ (2 mL) solution of DMAP (0.29 g, 2.35 mmol) was slowly added to $ClMe_2P{=}NSiMe_3$ (**9a**) (0.43 g, 2.35 mmol) in $CHCl_3$ (2 mL). The resulting clear and colorless solution was stirred for 1 h and the product [**10a**]Cl was characterized in solution. All volatiles were then removed in vacuo which afforded a viscous clear and colorless oil. The oil was redissolved in CH_2Cl_2 (0.5 mL) and was recrystallized at $-30\,^\circ$C by Et_2O vapor diffusion, yielding a white crystalline solid (0.58 g, 81%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=26.7$ ppm (s); ^1H NMR ($CDCl_3$): $\delta=0.00$ (s, 9H; $SiMe_3$), 2.09 (d, $^2J_{H,P}=13.8$ Hz, 6H; P–Me), 3.28 (s, 6H; NMe_2), 6.95 (d, $J=7.7$ Hz, 2H; *m*-H, DMAP), 9.17 ppm (t, $J=8.3$ Hz, 2H; *o*-H, DMAP); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta=3.0$ (s; $SiMe_3$), 20.2 (d, $^1J_{C,P}=79.6$ Hz; P–Me), 40.4 (s; NMe_2), 107.5 (s; *m*-C, DMAP), 140.5 (s; *o*-C, DMAP), 156.9 ppm (s; *p*-C, DMAP); elemental analysis calcd (%) for $C_{12}H_{25}N_3ClPSi$ (305.86): C 47.12, H 8.24, N 13.74; found: C 46.48, H 8.37, N: 14.33; redissolving crystals of [**10a**]Cl in $CDCl_3$ resulted in the partial dissociation of the salt to the parent phosphoranimine $ClMe_2P{=}NSiMe_3$ (**9a**) ($^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=24.1$ ppm (30%)) and free DMAP.

[DMAP·PMe$_2$=NSiMe$_3$]Br [10a]Br: A solution of DMAP (0.12 g, 0.99 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $BrMe_2P{=}NSiMe_3$ (**11a**) (0.23 g, 0.99 mmol) in CH_2Cl_2 (5 mL). The clear and colorless solution was allowed to stir for 1 h and then all volatiles were removed yielding a white crystalline solid. The crude product was purified by slow vapor diffusion of Et_2O onto a saturated CH_3CN solution in which clear and colorless crystals suitable for a single crystal X-ray diffraction study were grown (0.32 g, 92%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=27.4$ ppm (s); ^1H NMR ($CDCl_3$): $\delta=0.05$ (d, $^4J_{H,P}=0.6$ Hz, 9H; $SiMe_3$), 2.15 (d, $^2J_{H,P}=13.8$ Hz, 6H; P–Me), 3.29 (s, 6H; NMe_2), 6.95 (d, $J=7.8$ Hz, 2H; *m*-H, DMAP), 9.17 ppm (t, $J=8.1$ Hz, 2H; *o*-H, DMAP); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta=3.5$ (d, $^3J_{C,P}=4.9$ Hz; $SiMe_3$), 21.0 (d, $^1J_{C,P}=79.6$ Hz; P–Me), 40.9 (s; NMe_2), 108.0 (d, $^3J_{C,P}=3.5$ Hz; *m*-C, DMAP), 141.2 (d, $^2J_{C,P}=6.0$ Hz; *o*-C, DMAP), 157.5 ppm (s; *p*-C, DMAP).

[DMAP·PMePh=NSiMe$_3$]OTf [10b]OTf: A solution of either $ClMePhP{=}NSiMe_3$ (**9b**) or $BrMePhP{=}NSiMe_3$ (**11b**) (1.35 mmol) in $CHCl_3$ (5 ml) was added to a stirring suspension of DMAP (0.16 g, 1.35 mmol) and AgOTf (0.35 g, 1.35 mmol) in $CHCl_3$. The mixture was stirred for 2 h and the white/silver salt was filtered. The filtrate was reduced to dryness and the residual solid was recrystallized from Et_2O vapor diffusion onto a saturated solution of [**10b**]OTf $-30\,^\circ$C (0.40 g, 62%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=15.9$ ppm (s); ^1H NMR ($CDCl_3$): $\delta=0.02$ (s, 9H; $SiMe_3$), 2.27 (d, $^2J_{H,P}=13.5$ Hz, 3H; P–Me), 3.20 (s, 6H; NMe_2), 6.91 (d, $J=7.5$ Hz, 2H; *m*-H, DMAP), 7.43–7.56 (m; Ph), 7.72–7.80 (m; Ph), 8.38 ppm (t, $J=7.5$ Hz, 2H; *o*-H, DMAP); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta=3.1$ (d, $^3J_{C,P}=3.1$ Hz; $SiMe_3$), 17.1 (d, $^1J_{C,P}=82.0$ Hz; P–Me), 40.4 (s; NMe_2), 108.1 (d, $^3J_{C,P}=4.6$ Hz; *m*-C, DMAP), 120.8 (q, $^1J_{C,F}=320.5$ Hz; OTf), 129.3 (d, $^3J_{C,P}=14.6$ Hz; *m*-C, Ph), 130.4 (d, $^2J_{C,P}=12.3$ Hz; *o*-C, Ph), 130.5 (d, $^1J_{C,P}=122.0$ Hz; *i*-C, Ph), 133.5 (d, $^4J_{C,P}=2.3$ Hz; *p*-C, Ph), 139.5 (d, $^2J_{C,P}=5.3$ Hz; *o*-C, DMAP), 157.3 ppm (s; *p*-C, DMAP); ^{19}F NMR ($CDCl_3$): $\delta=-78.2$ ppm (s; OTf); elemental analysis calcd for $C_{18}H_{27}N_3F_3O_3PSSi$ (481.55): C 44.90, H 5.65, N 8.73; found: C 43.71, H 5.53, N 8.70.

Reaction between ClMePhP=NSiMe$_3$ (9b) and DMAP: A solution of DMAP (0.18 g, 1.46 mmol) in $CDCl_3$ (5 mL) was added to a solution of $ClMePhP{=}NSiMe_3$ (**9b**) (0.35 g, 1.46 mmol) in $CDCl_3$ (2 mL). The resulting clear and colorless solution was allowed to stir for 1 h, after which the $^{31}P\{^1H\}$ NMR spectrum was recorded. Two species were observed in solution; **9b** ($^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=16.5$ ppm (88%)) and the de-

sired salt [**10b**]Cl ($^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 17.1$ ppm (12%)). No changes were observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution after 24 h of stirring.

[DMAP·PMePh=NSiMe$_3$]Br [10b]Br: A solution of DMAP (0.16 g, 1.33 mmol) in CH_2Cl_2 (5 mL) was added to a solution of BrMePhP=NSiMe$_3$ (**11b**) (0.39 g, 1.33 mmol) in CH_2Cl_2 (5 mL). The clear and colorless solution was allowed to stir for 1 h and then all volatiles were removed, yielding a white crystalline solid. The crude product was purified by slow vapor diffusion of Et_2O onto a saturated CH_3CN solution in which clear and colorless crystals suitable for a single-crystal X-ray diffraction study were grown (0.32 g, 92%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 15.9 ppm (s); ^1H NMR ($CDCl_3$): $\delta = 0.01$ (d, $^4J_{H,P} = 0.6$ Hz, 9H; $SiMe_3$), 2.25 (d, $^2J_{H,P} = 13.5$ Hz, 3H; P–Me), 3.24 (s, 6H; NMe_2), 6.96 (d, $J =$ 7.5 Hz, 2H; *m*-H, DMAP), 7.38–7.52 (m; Ph), 7.88–7.95 (m; Ph), 8.38 ppm (t, $J = 7.5$ Hz, 2H; *o*-H, DMAP). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 3.1$ (d, $^3J_{C,P} = 3.4$ Hz; $SiMe_3$), 18.0 (d, $^1J_{C,P} = 79.6$ Hz; P–Me), 40.8 (s; NMe_2), 108.0 (d, $^3J_{C,P} = 4.0$ Hz; *m*-C, DMAP), 129.1 (d, $^2J_{C,P} = 14.3$ Hz; *o*-C, Ph), 130.4 (d, $^1J_{C,P} = 122.0$ Hz; *i*-C, Ph), 130.5 (d, $^3J_{C,P} = 12.3$ Hz; *m*-C, Ph), 133.2 (d, $^4J_{C,P} = 2.9$ Hz; *p*-C, Ph), 140.1 (d, $^2J_{C,P} = 6.0$ Hz; *o*-C, DMAP), 157.0 (s; *p*-C, DMAP).

Reaction between ClPh$_2$P=NSiMe$_3$ (9c) and DMAP: A solution of DMAP (0.23 g, 1.86 mmol) in $CDCl_3$ (5 mL) was added to a solution of **9c** (0.57 g, 1.86 mmol) in $CDCl_3$ (2 mL). The resulting clear and colorless solution was allowed to stir for 1 h, after which the $^{31}P\{^1H\}$ NMR spectrum was recorded. Two species were observed in solution, **9c** ($^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.8$ ppm (63%)) and the desired salt [**10c**]Cl ($^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 11.9$ ppm (37%)). No changes were observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution after 28 h of stirring.

[DMAP·PPh$_2$=NSiMe$_3$]OTf [10c]OTf: In an amber vial, a mixture of DMAP (0.11 g, 0.86 mmol) and AgOTf (0.22 g, 0.86 mmol) was suspended in $CDCl_3$ (3 mL). A solution of ClPh$_2$P=NSiMe$_3$ (**9c**) (0.27 g, 0.86 mmol) in $CDCl_3$ was quickly added to the stirring suspension. The reaction mixture was allowed to stir in the dark for 24 h. The white precipitate was filtered and the solvent was removed from the filtrate in vacuo which resulted in a tacky white solid. The residue was recrystallized from Et_2O vapor diffusion into a saturated $CHCl_3$ solution (0.36 g, 92%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.8$ ppm (s); ^1H NMR ($CDCl_3$): $\delta =$ -0.09 (d, $^4J_{H,P} = 0.6$ Hz, 9H; $SiMe_3$), 3.27 (s, 6H; NMe_2), 6.99 (d, $J =$ 7.8 Hz, 2H; *m*-H, DMAP), 7.49–7.65 (m; Ph), 8.14 ppm (t, $J = 7.8$ Hz, 2H; *o*-H, DMAP); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 3.1$ (d, $^3J_{C,P} = 3.8$ Hz; $SiMe_3$), 40.9 (s; NMe_2), 108.4 (d, $^3J_{C,P} = 4.6$ Hz; *m*-C, DMAP), 121.0 (q, $^1J_{C,F} = 321.3$ Hz; OTf), 128.5 (d, $^1J_{C,P} = 122.6$ Hz; *i*-C, Ph), 129.6 (d, $^2J_{C,P} =$ 13.7 Hz; *o*-C, Ph), 132.0 (d, $^3J_{C,P} = 11.5$ Hz; *m*-C, Ph), 133.9 (d, $^4J_{C,P} =$ 3.0 Hz; *p*-C, Ph), 140.0 (d, $^2J_{C,P} = 6.1$ Hz; *o*-C, DMAP), 157.7 ppm (s; *p*-C, DMAP); ^{19}F NMR ($CDCl_3$): $\delta = -78.2$ ppm (s; OTf).

In situ preparation of Cl(CF$_3$CH$_2$O)$_2$P=NSiMe$_3$ (9d): A solution of SO_2Cl_2 (0.11 g, 0.80 mmol) in $CDCl_3$ (2 mL) was added dropwise to a solution of $(CF_3CH_2O)_2PN(SiMe_3)_2$ (0.31 g, 0.80 mmol) in $CDCl_3$ (5 mL) cooled in an ice bath. Upon complete addition of SO_2Cl_2, the ice bath was removed and the clear colorless solution was stirred for 1 h. The resulting reaction mixture was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy and indicated a quantitative yield of **9d**. The reaction mixture was stored at -30 °C without significant decomposition. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta =$ -15.6 ppm; ^1H NMR ($CDCl_3$): $\delta = 0.17$ (d, $^4J_{H,P} = 1.5$ Hz; $SiMe_3$), 0.49 (s; $ClSiMe_3$), 4.42 ppm (d of pentets, $^3J_{H,P} = 2.1$, $^3J_{H,F} = 7.8$ Hz; OCH_2CF_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 2.3$ (d, $^3J_{C,P} = 5.1$ Hz; $SiMe_3$), 3.4 (s; $ClSiMe_3$), 64.1 (d of q, $^2J_{C,P} = 6.3$, $^2J_{CF} = 38.2$ Hz; O*C*H$_2$CF$_3$), 122.4 ppm (d of q, $^3J_{C,F} = 12.3$, $^1J_{C,F} = 277.4$ Hz; OCH$_2$*C*F$_3$); ^{19}F NMR ($CDCl_3$): $\delta =$ -74.9 ppm (t, $^3J_{F,H} = 7.6$ Hz; OCH_2CF_3); $^{29}Si\{^1H\}$ NMR ($CDCl_3$): $\delta =$ -4.4 ppm (d, $^2J_{Si,P} = 22.9$ Hz; $SiMe_3$), 31.1 ppm ($ClSiMe_3$).

[DMAP·P(OCH$_2$CF$_3$)$_2$=NSiMe$_3$]OTf [10d]OTf: A solution of **11d** (0.61 g, 1.54 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a mixture of DMAP (0.19 g, 1.54 mmol) and AgOTf (0.40 g, 1.56 mmol) in CH_2Cl_2 (10 mL) at 25 °C (in the absence of light). A white precipitate formed immediately and the reaction was stirred for 30 min. The reaction mixture was then filtered and solvent removed in vacuo, resulting in white solid. Recrystallization from a CH_2Cl_2/hexanes mixture afforded large colorless plates of [**10d**]OTf (0.74 g, 82%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -21.9$ ppm (s); ^1H NMR ($CDCl_3$): $\delta = 0.16$ (d, $^3J_{H,P} = 0.6$ Hz, 9H; $SiMe_3$), 3.35 (s, 6H; NMe_2), 4.46 (d of pentets, $^3J_{H,P} = 8.1$, $^3J_{HF} = 11.7$ Hz, 4H; OCH_2CF_3), 6.99 (dd, $J_{H,H} = 2.1$, 8.1 Hz, 2H; *m*-H, DMAP), 8.12 ppm (dd, $J_{H,H} = 8.1$, 8.4 Hz, 2H; *o*-H, DMAP); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 2.6$ (d, $^3J_{C,P} =$ 3.5 Hz; $SiMe_3$), 41.1 (s; NMe_2), 64.3 (d of q, $^2J_{C,P} = 4.6$, $^2J_{C,F} = 38.3$ Hz; O*C*H$_2$CF$_3$), 108.6 (d, $^3J_{C,P} = 8.0$ Hz; *m*-C, DMAP), 120.85 (q, $^1J_{C,F} =$ 320.1 Hz; OTf), 122.3 (d of q, $^3J_{C,P} = 8.9$, $^1J_{C,F} = 277.8$ Hz; OCH_2CF_3), 140.2 (d, $^2J_{C,P} = 5.4$ Hz; *m*-C, DMAP), 158.1 ppm (s; *p*-C, DMAP); ^{19}F NMR ($CDCl_3$): $\delta = -78.5$ (s; OTf), -74.9 ppm (t, $^3J_{F,H} = 7.9$ Hz; OCH_2CF_3); ESIMS (70 eV): *m*/*z* (%): 438.1195 $[M-OTf]^+$; elemental analysis calcd (%) for $C_{15}H_{23}F_9N_3O_5PSSi$ (587.5): C 30.66, H 3.95, N 7.15; found: C 30.21, H 3.81, N 7.48.

[DMAP·P(OCH$_2$CF$_3$)$_2$=NSiMe$_3$]SO$_2$Cl [10d]Cl·SO$_2$: A freshly prepared solution of **9d** (2.82 mmol) in CH_2Cl_2 (15 mL) was added slowly to a solution of DMAP (0.34 g, 2.82 mmol) in CH_2Cl_2 (10 mL). The resulting yellow solution was stirred for 30 min and reduced to dryness yielding a pale-yellow solid. Recrystallization from a CH_2Cl_2/hexanes mixture yielded clear colorless crystals of [**10d**]Cl·SO_2 (0.93 g, 61%); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -21.8$ ppm (s); ^1H NMR ($CDCl_3$): $\delta = 0.26$ (s, 9H; $SiMe_3$), 3.52 (s, 6H; NMe_2), 4.62 (d of pentets, $^3J_{H,P} = 7.8$, $^3J_{H,F} = 12.0$ Hz, 4H; OCH_2CF_3), 7.28 (dd, $J = 2.4$, 8.4 Hz, 2H; *m*-H, DMAP), 8.37 ppm (t, $J =$ 8.1 Hz, 2H; *o*-H, DMAP); ^{19}F NMR ($CDCl_3$): $\delta = -74.7$ ppm (t, $^3J_{F,H} =$ 8.5 Hz; OCH_2CF_3).

DMAP·SO$_2$ 12: A solution of DMAP (2.04 g, 17.10 mmol) in CH_2Cl_2 (50 mL) was bubbled with SO_2 gas for 15 min at ambient temperature. The resulting yellow suspension was filtered and all volatiles were removed from the yellow filtrate yielding **12** as a white crystalline solid (2.83 g, 91%). ^1H NMR ($CDCl_3$): $\delta = 3.05$ (s, 6H; NMe_2), 6.52 (dd, $J =$ 1.5, 5.7 Hz, 2H; *m*-H, DMAP), 8.19 ppm (dd, $J = 1.5$, 5.7 Hz, 2H; *o*-H, DMAP); ^{13}C NMR ($CDCl_3$): $\delta = 39.7$ (s; NMe_2), 106.5 (s; *m*-C, DMAP), 142.4 (s; *m*-C, DMAP), 155.7 ppm (s; *p*-C, DMAP); EIMS (70 eV) *m*/*z* (%): 121 (100) $[DMAP]^+$, 64 (68) $[SO_2]^+$.

[DMAP·P(OCH$_2$CF$_3$)$_2$=NSiMe$_3$]Br [10d]Br: A solution of DMAP (1.74 g, 14.2 mmol) in CH_2Cl_2 (5 mL) was added to a solution of **11d** (5.63 g, 14.2 mmol) in CH_2Cl_2 (5 mL) at 25 °C. The resulting clear, colorless solution was stirred for 1 h and then reduced to dryness resulting in a white crystalline solid (7.19 g, 98%). Recrystallization of the solid from a CH_2Cl_2/hexanes mixture yielded clear colorless crystals suitable for single-crystal X-ray diffraction. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -21.8$ ppm (s); ^1H NMR ($CDCl_3$): $\delta = 0.18$ (s, 9H; $SiMe_3$), 3.48 (s, 6H; NMe_2), 4.53 (d of pentets, $^3J_{H,P} = 7.8$, $^3J_{H,F} = 12.0$ Hz, 4H; OCH_2CF_3), 7.28 (dd, $J = 2.4$, 8.4 Hz, 2H; *m*-H, DMAP), 8.24 ppm (t, $J = 8.1$ Hz, 2H; *o*-H, DMAP); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 2.4$ (d, $^3J_{C,P} = 3.5$ Hz; $SiMe_3$), 41.6 (s; NMe_2), 64.3 (d of q, $^2J_{C,P} = 4.9$, $^2J_{C,F} = 38.1$ Hz; O*C*H$_2$CF$_3$), 108.9 (d, $^3J_{C,P} = 8.0$ Hz; *m*-C, DMAP), 121.9 (d of q, $^3J_{C,P} = 8.3$ $^1J_{C,F} = 278.2$ Hz; OCH$_2$*C*F$_3$), 140.0 (d, $^2J_{C,P} = 5.7$ Hz; *o*-C, DMAP), 157.5 ppm (s; *p*-C, DMAP); ^{19}F NMR ($CDCl_3$): $\delta = -74.7$ ppm (t, $^3J_{F,H} = 8.5$ Hz; OCH_2CF_3); elemental analysis calcd (%) for $C_{14}H_{23}F_6BrN_3O_2PSi$ (518.3): C 32.44, H 4.47, N 8.11; found: C 32.84, H 4.43, N 8.20.

Preparation of [DMAP·P(OCH$_2$CF$_3$)$_2$=NSiMe$_3$]BF$_4$ [10d]BF$_4$: A solution of **11d** (0.37 g, 0.93 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a suspension of DMAP (0.11 g, 0.93 mmol) and $AgBF_4$ (0.18 g, 0.93 mmol) in CH_2Cl_2 (10 mL) at 25 °C (in the absence of light). A brown precipitate formed after stirring for 30 min. The brown suspension was filtered and the solvent removed in vacuo, yielding a pale-yellow oil. Recrystallization from a CH_2Cl_2/hexanes mixture afforded large colorless plates of [**10d**]BF_4 (0.38 g, 77%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -22.0$ ppm (s); ^1H NMR ($CDCl_3$): $\delta = 0.17$ (d, $^3J_{H,P} = 0.9$ Hz, 9H; $SiMe_3$), 3.34 (s, 6H; NMe_2), 4.46 (d of pentets, $^3J_{H,P} = 7.8$, $^3J_{H,F} = 11.4$ Hz, 4H; OCH_2CF_3), 6.96 (dd, $J_{H,H} = 2.4$, 8.1 Hz, 2H; *m*-H), 8.12 ppm (t, $J_{H,H} = 8.1$ Hz, 2H; *o*-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 2.6$ (d, $^3J_{C,P} = 3.5$ Hz; $SiMe_3$), 41.1 (s; NMe_2), 64.3 (d of q, $^2J_{C,P} = 4.6$, $^2J_{C,F} = 38.3$ Hz; O*C*H$_2$CF$_3$), 108.5 (d, $^2J_{C,P} = 8.0$ Hz; *o*-C), 122.3 (d of q, $^3J_{C,P} = 9.1$, $^1J_{C,F} = 277.8$ Hz; OCH$_2$*C*F$_3$), 140.2 (d, $^3J_{C,P} = 5.4$ Hz; *m*-C), 158.1 ppm (s; *p*-C); ^{19}F NMR ($CDCl_3$): $\delta = -152.6$ (s, BF_4), -74.8 ppm (t, $^3J_{F,H} = 7.6$ Hz; OCH_2CF_3); $^{29}Si\{^1H\}$ NMR ($CDCl_3$): $\delta = -3.8$ ppm (d, $^2J_{Si,P} = 26.5$ Hz); $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta = -1.5$ ppm (s; BF_4); m.p. 93–95 °C; EIMS (70 eV): *m*/*z* (%): 507 $[M-F]^+$, 264 (26)

$[M-BF_4-SiMe_3-CF_3CH_2O]^+$, 123 (100) $[DMAPH]^+$; ESIMS (70 eV), *m/z* (%): 438.1195 $[M-BF_4]^+$; elemental analysis calcd (%) for $C_{14}H_{23}F_{10}N_3O_2BPSi$ (525.2): C 32.02, H 4.41, N 8.00; found: C 31.93, H 4.33, N 8.24.

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