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Phosphazene-Based Ionic Liquids: Synthesis, Temperature-Dependent Viscosity, and Effect as Additives in Water Lubrication of Silicon Nitride Ceramics

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Phosphazene rings with (dimethylamino)ethoxy (**1**, **2**), pyridylmethoxy (**3**), or (dimethylamino)propoxy (**4**) chains were synthesized and quaternized at the substitutent nitrogen by treatment with methyl iodide at 35 °C over 3–6 h to give polyiodo salts, **5**–**8**. Subsequent metathesis with $LiN(SO_2CF_3)_2$ or $NaBF_4$ gave the respective ionic salts, **9**–**13**. The amide salts, **9**–**12**, were viscous liquids with pour points at 55–100 °C, and the tetrafluoroborate salt, **13**, was a solid, mp 168 °C. The compositions of **2** and **5**–**13** were confirmed by elemental analysis and spectroscopic methods. Compounds **1**, **2**, and **4** were viscous liquids ($d_{25} = 1.67$ g cm^{-3}; $\eta_{25} = 0.76$–1.56 mPa s^{-1}) with pour points at ∼15 °C. The solid polyquaternary salts, **5**–**8**, melted at 130–194 °C. The ionic liquids, **9**–**12**, had an average density of ∼1.73 g cm^{-3} at 25 °C, and viscosities (25 °C) ranged between 68.3 and 139.2 mPa s^{-1}. A plot of the viscosities of **9**–**12** vs temperature revealed an almost linear correlation between 55 and 120 °C. Friction and wear properties of water with 0.25 wt % of **9**–**12** as boundary lubricant additives were evaluated on Si_3N_4/Si_3N_4 ceramic interfaces. The most significant observation is that they caused a decrease in the running-in period.

Introduction

Ionic liquids are a class of compounds with very useful materials properties.[1–5] According to a specialized study, the tribological properties of some imidazolium tetrafluoroborates[6,7] compared favorably with those of poly(fluoroaryloxy) phosphazenes that are excellent lubricants for aircraft gas turbine engines.[8,9] The pour points for the ionic liquids were ∼−50 °C, and they were excellent candidates for vacuum lubrication. They also had good potential for lubrication of steel/steel, steel/aluminum, and steel/copper contacts, exhibiting friction reduction, antiwear properties, and heavy load-carrying capacity.[6,7] Generally, the friction coefficient of ionic liquid/water mixtures on Si_3N_4, determined from a pin-on-disk tribometer,[10] was reported to drop to less than 0.1 within hundreds of cycles. Water alone required 8000−9000 cycles to achieve the same results and produced more wear.[10] It was also reported that, in a comparison of the lubricity of the 2 wt % ionic liquids in water, $emim^+PF_6^-$ solution transitioned to low friction quicker than the $emim^+BF_4^-$.

We were interested in the correlation of ionic liquid chemistry to their tribological properties. The tris(trimethylammonium)- and tris(imidazolium)triamide salts[12] were more

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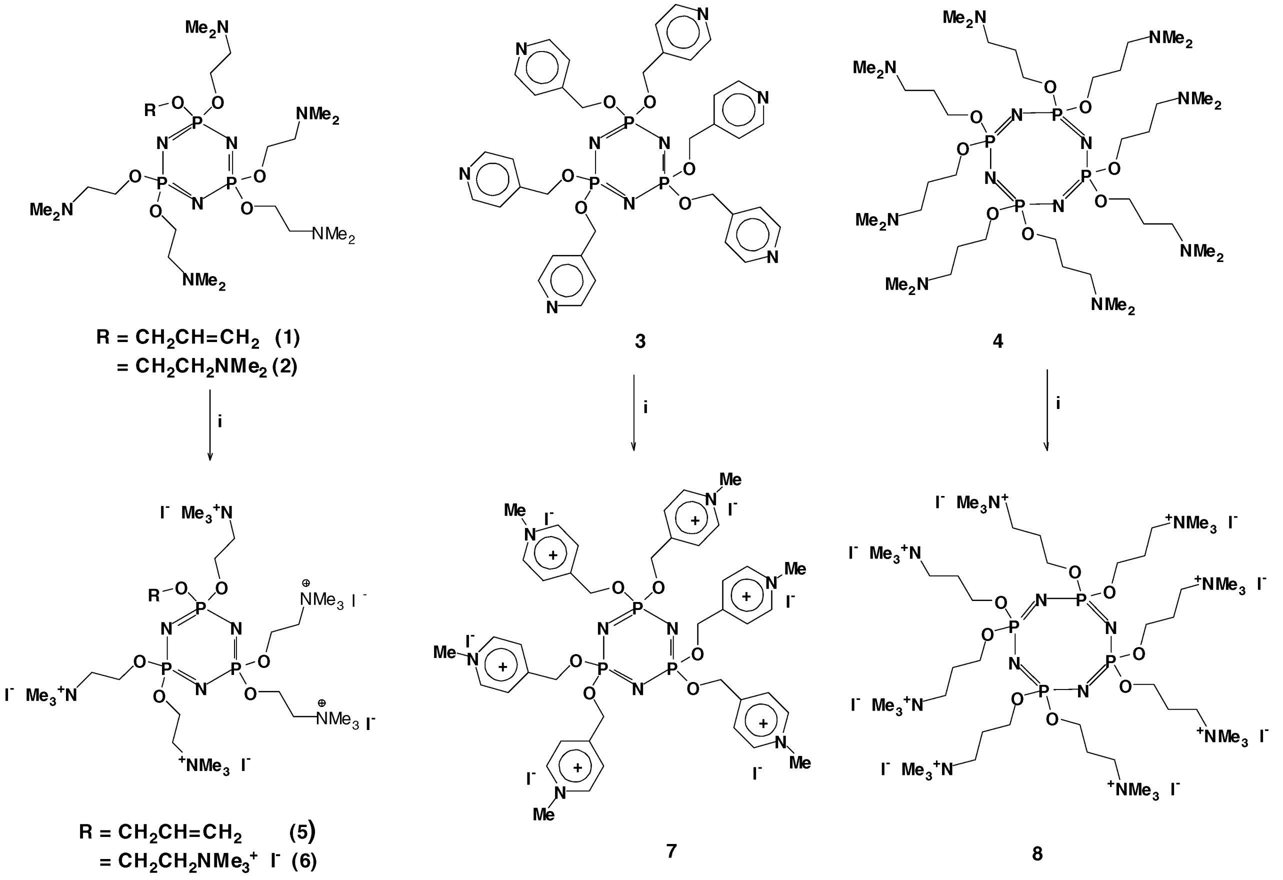
Scheme 1



i. MeI/ EtOH/25 °C/6 h

viscous than the amide salt, emim$^+$NTf$_2^-$.[11] Therefore, the synthesis of even more viscous polyquaternary ionic liquids was of interest to us for this purpose, and the following phosphazene-based compounds were prepared in this work: hexakis(trimethylammonium) (**9**), pentakis(trimethylammonium) (**10**), hexakis(*N*-methylpyridinium) (**11**), and octakis(trimethylammonium) phosphazene (**12**) poly[bis(trifluoromethanesulfonyl)amide]. Essentially, this paper describes the syntheses, characterization, and physical, thermal, and tribological properties of phosphazene-based poly(trimethylammonium) and poly(*N*-methylpyridinium) ionic liquids.

Results and Discussion

There are very few stable ionic phosphazene compounds in the literature because such compounds are very reactive and often undergo thermally induced decomposition.[13] While the synthesis of **3**, a white solid, was reported in the literature,[14] we obtained the ^{13}C NMR spectral data, which consist of signals at 66.7 (dd, $J = 3$ Hz, $J = 2$ Hz), 121.9, 145.8 (dd, $J = 5$ Hz, $J = 3$ Hz), and 150.5 ppm. Compounds **1**, **2**, and **4** were obtained as colorless viscous liquids from metathesis reactions of the sodium salt of either *N*,*N*-dimethylethan-2-ol or *N*,*N*-dimethylpropan-3-ol and the respective polychlorophosphazene. They were characterized by multinuclear NMR and infrared spectroscopy. Elemental analysis indicated that **2** was isolated as a pentahydrate. The light yellow or brown compounds **5**−**8** were synthesized in almost quantitative yields from the reactions of **1**−**4** with excess of methyl iodide at room temperature (Scheme 1). On the basis of elemental analysis, they were isolated as hydrate salts. They were characterized by their NMR spectral data through comparison with the spectra of closely related compounds.[12−14] The compounds appeared to be very hygroscopic and were dried under dynamic vacuum (~0.8 Torr) at 40 °C for several days. However, upon exposure to the laboratory environment and especially on shipment and handling by our chemical analysts in China, it was impossible to maintain them in an anhydrous state. This is supported by the presence of a water band at ~3480 cm^{-1} in the IR spectra even after modest exposure to the ambient air.

At 25 °C, the physical state of ionic liquids with a common organic cation is often dependent on the anion; e.g., compounds with trifluoromethylsulfonate (OTf$^-$), hexafluorophosphate (PF$_6^-$), and tetrafluoroborate (BF$_4^-$) as counterions are usually isolated as solids, whereas the presence of the bis(trifluoromethanesulfonyl)amide anion (NTf$_2^-$) gives rise to liquids or solids.[11,12] To avoid the formation of

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Scheme 2

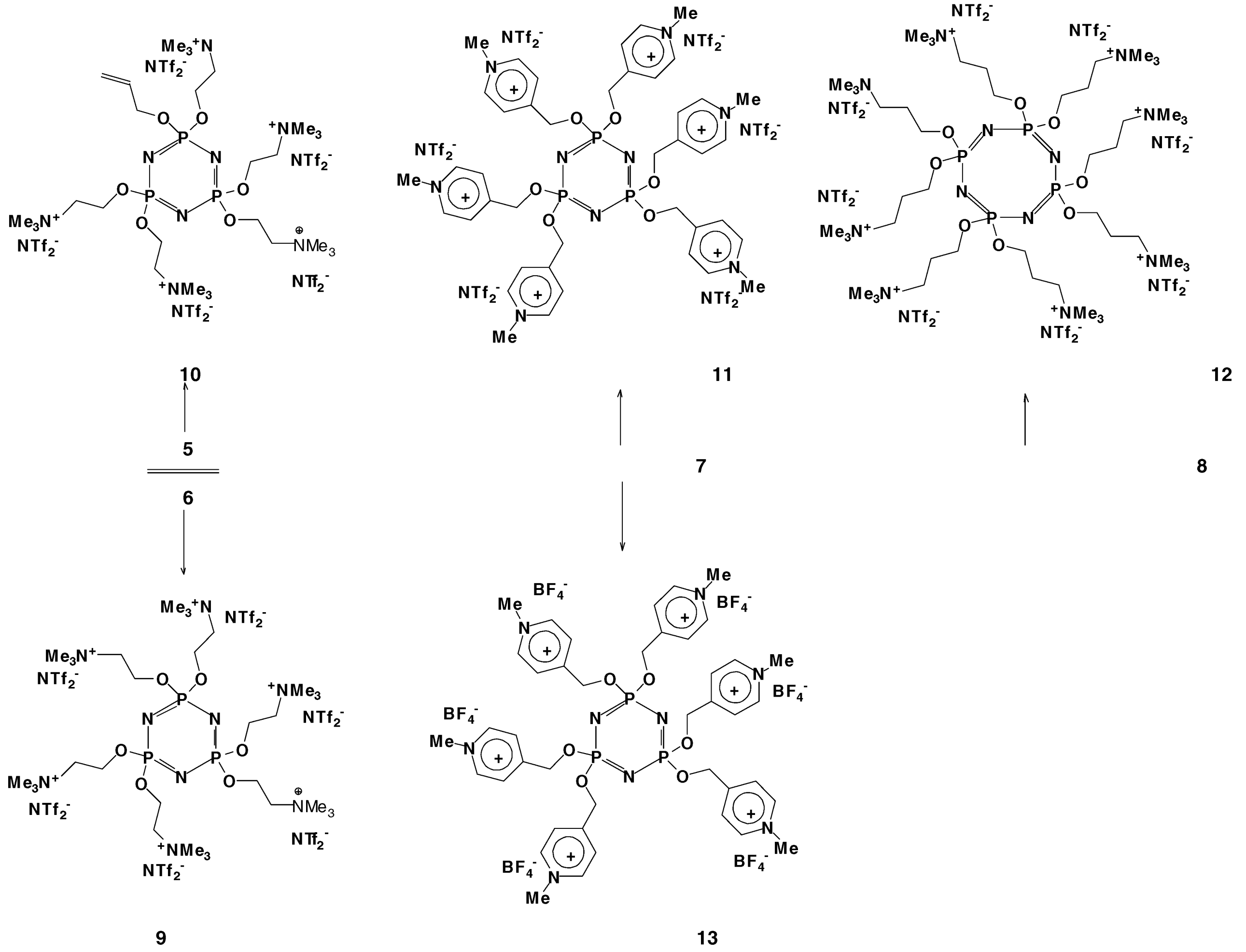

Table 1. Physical and Thermal Properties of the Poly(alkoxydimethylamino) and Poly(methoxypyridyl) Phosphazenes, **1−4**

			thermal data				
	phys properties		DSC			pour pt viscosity	
compd	state	density[a]	T_d[d]	T_g[e]	TGA[b]	°C	η[c]
1	liquid	1.63	313	−1	100	10	1.02
2	liquid	1.65	240		99	10	1.25
3	solid	*f*	224		99		
4	liquid	1.63	254		100	25	1.6

[a] g cm^{-3}. [b] Percentage of original mass at temperature corresponding to T_d in DSC. [c] Determined by drop-ball method (Pa s^{-1}). [d] Decomposition temperature in °C. [e] Glass transition temperature in °C. [f] Reference 12.

high melting solids, efforts to form low melting polyquaternary ionic liquids were concentrated on obtaining the NTf_2^- derivatives of **5−8**. This was achieved by the familiar metathesis reactions of aqueous solutions of the respective polyiodo ionic compounds and $LiNTf_2$ at between 25 and 30 °C with a reaction time of ~1 h, resulting in the isolation of anhydrous and hydrophobic products, **9−12** (Scheme 2). One tetrafluoroborate salt, **13**, was formed via the room-temperature reaction of an aqueous solution of **7** and sodium tetrafluoroborate. While compounds **5−8** and **13** are water-soluble ionic solids, **9−12** are not. Although **5−13** are soluble in very polar organic solvents such as acetonitrile and ethyl acetate, **9−12** are only moderately soluble in less polar solvents, such as dichloromethane and chloroform.

Physical Properties. The density, pour point, viscosity, and thermal properties of **1−4** are summarized in Table 1. With the exception of **3** that is a solid, these completely alkoxy-substituted phosphazenes had densities of ~1.65 g cm^{-3}, viscosities between 1 and 1.6 Pa s^{-1} at 25 °C, and pour points between 10 and 25 °C. According to the DSC thermograms, all four compounds were thermally stable to >200 °C, and **1** showed a glass transition temperature of −1 °C.

The physical and thermal stability data for the ionic compounds, **5−13**, obtained from differential scanning calorimetry (DSC) and thermogravimetry (TGA) are summarized in Table 2. The amide salts were either viscous liquids or waxy solids at 25 °C. While the polyiodides, **5−8**,

Table 2. Physical and Thermal Properties of the Poly(trimethylammonium)- and Poly(*N*-methoxypyridinium)phosphazene Salts, **5−13**

			thermal data								
	phys properties		DSC				viscosity (Pa s^{-1})^a				
compd	state	Mp (°C) (density)^b	T_d^{d}	T_m^{e}	TGA^c	pour pt (40 °C)	55 °C	70 °C	85 °C	100 °C	120 °C
5	solid	152	200	162	99						
6	solid	194	216	227	100						
7	solid	130	196	146	98						
8	solid	168	316	186	99						
9	liquid	(1.68)	290		98	55	139.2	23.32	16.26	9.44	2.18
10	wax	(1.7)^f	230		100	70	62.83	15.82	11.64	6.95	2.12
11	liquid	(1.78)	326	−21^g	100	70	114.7	40.88	29.97	18.5	3.37
12	liquid	(1.72)	246		100	100	112.7	31.4	23.4	15.4	2.49
13	solid	168	330		100						

^{a} Determined by sheer method. ^{b} g cm^{-3} (at 25 °C). ^{c} Percentage of original mass at temperature corresponding to T_d in DSC. ^{d} Decomposition temperature in °C. ^{e} Phase transition temperature in °C. ^{f} 70 °C. ^{g} Glass transition temperature in °C (T_g).

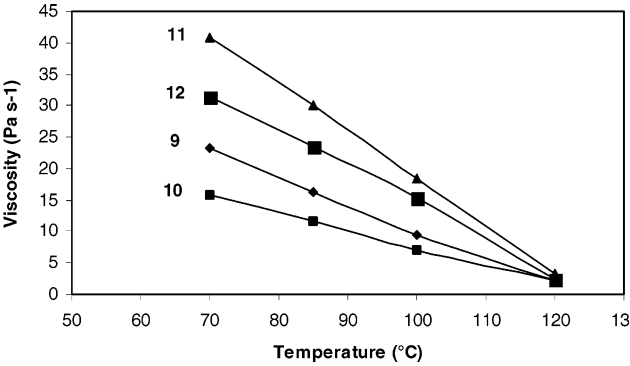

Figure 1. Temperature-dependent viscosity data for **9−12** between 70 and 120 °C.

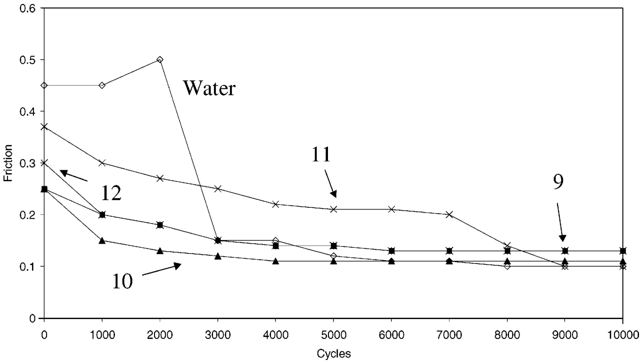

Figure 2. Water and **9−12** friction traces on rough Si_3N_4 from a pin-on-disk tribometer (sample roughness = 0.3 μm).

were solids with a range of melting points between 130 and 194 °C, **9−12** are liquid salts. The pour points for **9−11** were about 55 °C, and the value was 100 °C for **12**. The viscosities for the four compounds were measured at different temperatures between 55 and 120 °C. Viscosity decreased with increasing temperature and almost converged for the four compounds, to less than 1 Pa s^{-1} at 120 °C. The values were 2.1−139.2 Pa s^{-1} between 70 and 100 °C (Table 2), which is the typical range for industrial reaction temperatures.[15] The trend of viscosity in this temperature range is almost linear (Figure 1), but the data obtained at temperatures less than 70 °C do not present any trend. The results suggest that the compounds are free-flowing liquids between 70 and 120 °C. They were sticky and adhered to the glass wall strongly below these temperatures. The viscosity data showed a correlation with temperature within this temperature range.

Tribological Properties. Ionic liquids have been reported to have potential as lubricating oils and as boundary lubricants for water lubricated Si_3N_4. A plot of friction coefficient versus the film thickness parameter is called the Streibek curve.[10] This curve helps to illustrate that viscosity is an important factor that determines fluid lubrication. In addition, oils must be fluid and of the appropriate viscosity in the range of temperatures where they will be used. The ionic liquids, **9−12**, in this work were more viscous than the neutral compounds **1−4**. In fact, they were too viscous for use as oils. However, the case has been made for the use of ionic liquids (in water) as lubricant additives for Si_3N_4/Si_3N_4 interfaces.[10]

Since the work by Tomizawa and Fischer,[16] many have reported that water provided low friction lubrication of Si_3N_4 ceramics.[17] However, extensive wear of Si_3N_4 surfaces occurs during high friction run-in. The addition of ionic liquids to water significantly reduces the running in period.[10] The tribological properties of water with 0.25 wt % of **9−12** as boundary lubricant additives were evaluated on Si_3N_4 ceramics. All four ionic liquids showed improvement over water alone. The running-in period for Si_3N_4 was decreased in all cases (Figure 2). This behavior is similar to the work done by Phillips et al.[10] Using 1-methyl-3-*n*-butylimidazolium hexafluorophosphate and 1-ethyl-3-methylimidazolium tetrafluoroborate as additives to water, the running-in period of Si_3N_4 was decreased within a few hundred cycles as compared to over 5000 cycles for water alone. This response was partially attributed to the formation of an electric double layer on the surface, which increased the local viscosity and increased the load carrying capability. Comparing these results with the current work shows that the new ionic liquids

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did not transition to low friction as quickly as with the imidazolium salts.[10] Although the ionic liquids do lower the initial friction coefficient and running-in period of Si_3N_4, the slow transition to low friction may be attributed to the low solubility of these ionic liquids in water. The ionic liquid mixtures were originally targeted to produce a 2.0 wt % solution, because previous work showed that higher concentrations of ionic liquid improved the friction and wear response. However, the ionic liquids used in this study did not dissolve to produce a 2.0% solution. The solubility of these ionic liquids in water was 2.5 g/L ± 10%, which provided a 0.25 wt % solution. Use of ionic liquids with higher solubility may allow for a faster transition to low friction.

Conclusion

The synthesis of ionic phosphazene compounds in which the neutrality of the ring is preserved was achieved in this work. Their physical and thermal stability and temperature-dependent viscosity as well their tribological properties were also determined.

Experimental Section

General Considerations. Tetrahydrofuran (THF) and diethyl ether were dried with sodium and distilled over a purple benzophenone solution. The other chemicals used were obtained commercially from Aldrich, Acros, Lancaster, or Synquest. A standard Schlenk line system was used for handling the air- and moisture-sensitive reactions under nitrogen conditions. Infrared spectra were recorded on a Bio-Rad FTS 3000 Excalibur series infrared spectrometer as neat liquids between KBr plates. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were obtained on a Bruker AMX spectrometer (200, 300, or 500 MHz) by using $CDCl_3$ as locking solvent except where otherwise indicated. Chemical shifts are reported relative to Me_4Si, $CFCl_3$, or H_3PO_4. Differential scanning calorimetry (DSC) measurements were performed using a TA Instrument TA10 differential scanning calorimeter equipped with an auto-cool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooling from 40 to −80 °C and heating to 400 or 550 °C at 10 °C/min. Transition temperatures, T_m, were taken as peak maxima. Onset of decomposition was taken as when the abnormal section of the plot began. Thermogravimetric analysis (TGA) measurements were made using a TA Instrument TA50. Samples were heated at 10 °C/min from 25 to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min). Elemental analyses were performed by the Desert Analytics Laboratory, Tucson, AZ, and the SIOC, Shanghai, China. Density was determined using a pycnometer. Viscosity was obtained by either a drop-ball method (Minivis II) or a sheer method using a TA rheology instrument. The pour point reported is the temperature at which the sticky viscous materials became free flowing and could pour from a vial or a beaker.

Ionic Liquid Sample Preparation for Tribo-Testing. Four ionic liquids, **9**−**12**, were examined in this investigation. The 0.25 wt % solutions of the ionic liquids in water were evaluated in the tribology tests. The tribology tests used a self-mated Si_3N_4 contact. The surface roughness of the Si_3N_4 disk was 0.3 μm.

(a) Tribo-Testing. Friction and wear testing was performed using a pin-on-disk tribometer that utilizes a stationary 1/4 in. ball (Si_3N_4) on a 1 in. diameter rotating disk (Si_3N_4). Multiple runs of self-mated samples were performed on each disk with a constant linear speed constant of 0.120 m/s and a load of 1 N. The samples were run at room temperature in air for approximately 600 m.

(b) Synthesis. $N_3P_3(OCH_2CH{=}CH_2)(OCH_2CH_2NMe_2)_5{\cdot}xH_2O$ (1). To a suspension of the sodium salt of *N*,*N*-dimethylamino-2-ethanol [8.92 g (100 mmol)] in diethyl ether/pentane (1:1) formed from reaction with 2.4 g (100 mmol) of sodium hydride was slowly added a pentane solution of allyloxypentachlorotriphosphazene (5.54 g, 15 mmol).[18] A white precipitate formed. After being stirred at reflux for 3 h, the mixture was allowed to stand overnight, and the solid side product settled at the bottom of a clear solution. The solution was filtered and evaporated to give crude **1**. It was taken up in 10 mL of boiling pentane, and the warm solution was filtered. The filtrate was evaporated to dryness on a Rotavap.

IR: 3458 cm^{-1}, $\nu(H_2O)$. NMR ($CDCl_3$): ^1H, δ 2.25 [s, 30H, $P(OCH_2CH_2NMe_2)$], 2.58 (t, 10H, $CH_2CH_2NMe_2$), 3.92 (d, 2H, $OCH_2CH{=}CH_2$), 4.00 [s, 10h, $P(OCH_2CH_2NMe_2)$], 5.86 (m, 1H, $OCH_2CH{=}CH_2$), 6.10 (dd, 2H, $OCH_2CH{=}CH_2$); ^{13}C, δ 46.7 (NMe_2), 59.7 (d, J = 6 Hz) (CH_2NMe_2), 64.7 (d, J = 3 Hz) ($POCH_2$), 63.4 ($OCH_2CH{=}CH_2$), 119.1 ($OCH_2CH{=}CH_2$), 131.2 ($OCH_2CH{=}CH_2$); ^{31}P, δ 7.0 (t, J_{P-P} = 66 Hz, 1P), 19.1 ppm (d, J_{P-P} = 66 Hz, 2P).

$N_3P_3(OCH_2CH_2NMe_2)_6{\cdot}5H_20$ (2). Compound **2** was synthesized from reaction of hexachlorotriphosphazene by following the procedure described for **1.** IR: 3463 cm^{-1}, $\nu(H_2O)$. NMR ($CDCl_3$): ^1H, δ 2.25 [s, 36H, $P(OCH_2CH_2NMe_2)$], 2.58 (t, 12H, $CH_2CH_2NMe_2$), 4.00 [m, 12h, $P(OCH_2CH_2NMe_2)$]; ^{13}C, δ 46.7 (NMe_2), 59.7 (d, J = 6 Hz, CH_2NMe_2), 64.7 (d, J = 3 Hz, $POCH_2$); ^{31}P, δ 17.9 (s, 3P) ppm. Anal. Calcd for $C_{24}H_{70}N_9O_{11}P_3$: C, 38.25; H, 9.30; N, 16.73. Found: C, 37.49; H, 9.36; N, 17.22.

$N_3P_3(OCH_2pyr)_6$ (3). The synthesis of **3** and its NMR (^1H and ^{31}P) spectra as well as IR data and elemental analysis were described elsewhere.[13] However, because of P−C couplings observed in the ^{13}C NMR spectrum, the following previously unreported data are given. NMR ($CDCl_3$): ^{13}C, δ 66.7 (dd, J_{P-C} = 3 Hz, J_{P-C} = 2 Hz) ($POCH_2$), 121.9 (*m*-Ph), 145.8 (dd, J_{P-C} = 5 Hz, J_{P-C} = 3 Hz) (*o*-Ph), 150.5 (*p*-Ph) ppm; ^{31}P, δ 17.7 (s, 3P) ppm.

$N_4P_4(OCH_2CH_2CH_2NMe_2)_8{\cdot}xH_2O$ (4). To a suspension of the sodium salt of *N*,*N*-dimethylamino-2-propanol [10.3 g (100 mmol)] in diethyl ether/pentane (1:1) formed from its reaction with sodium hydride [2.4 g, 100 mmol)] was slowly added a pentane solution of octachlorotetraphosphazene. A gentle exotherm was observed as the two reagents made contact. A white precipitate formed. After being stirred at reflux for 3 h, the mixture was allowed to stand overnight, and the solid side product settled at the bottom of a clear solution. A syringe was used to remove the clear solution that was then evaporated to obtain **4** as a viscous brown liquid. IR: 3548 cm^{-1}, $\nu(H_2O)$. NMR ($CDCl_3$): ^1H, δ 1.82 (m, 16H, $CH_2CH_2CH_2NMe_2$), 2.20 [s, 48H, $P(OCH_2CH_2CH_2NMe_2)$], 2.44 (m, 16H, $CH_2CH_2CH_2NMe_2$), 3.93 [m, 16H, $P(OCH_2CH_2CH_2NMe_2)$]; ^{13}C, δ 45.7 (NMe_2), 48.6 ($CH_2CH_2CH_2NMe_2$), 61.1 ($CH_2CH_2CH_2NMe_2$), 66.3 ($POCH_2$) ppm; ^{31}P, δ 18.4 (s, 4P) ppm.

$N_3P_3(OCH_2CH_2NMe_3{}^+I^-)_5(OCH_2CH{=}CH_2){\cdot}10H_2O$ (5). To a stirring absolute ethanol solution of **1** was added 5.5 mol equiv of methyl iodide, and the mixture was held at reflux for 5 h. On cooling, **5** was precipitated with diethyl ether. Compound **5**, a brown powder, was removed by filtration and allowed to dry in a desiccator. Mp: 152 °C. IR: 3432 cm^{-1}, $\nu(H_2O)$. NMR ($CDCl_3$): ^1H, δ 2.44 (m, 10H, $CH_2CH_2NMe_3{}^+I^-$), 3.24 [s, 45H, $P(OCH_2CH_2NMe_3{}^+I^-)$], 3.96 [m, 10H, $P(OCH_2CH_2NMe_3{}^+I^-)$], 4.06 (d, 2H, $OCH_2CH{=}CH_2$), 5.20 (dd, 1H, $OCH_2CH{=}CH_2$), 5.95 ppm (dd,

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2H, $OCH_2CH{=}CH_2$); ^{13}C, δ 54.7 [$P(OCH_2CH_2NMe_3^+I^-)$], 61.0 [$P(OCH_2CH_2NMe_3^+I^-)$], 66.3 [$P(OCH_2CH_2NMe_3^+I^-)$] ppm; ^{31}P, δ 7.0 (t, $J_{P-P} = 66$ Hz, 1P), 19.1 ppm (d, $J_{P-P} = 66$ Hz, 2P). Anal. Calcd for $C_{28}H_{90}N_8O_{16}P_3I_5$: C, 22.08; H, 5.91; N, 7.36. Found: C, 21.88; H, 6.35; N, 7.78.

$N_3P_3(OCH_2CH_2NMe_3^+I^-)_6 \cdot 3H_2O$ (6). To a stirring absolute ethanol solution of **2** was an added 7 mol equiv of methyl iodide, and the mixture was held at reflux for 5 h. On cooling, the ionic product of the quaternization reaction was precipitated with diethyl ether. Compound **6**, a white powder, was filtered off and allowed to dry in a desiccator. Mp: 194 °C. IR: 3430 cm^{-1}, $\nu(H_2O)$. NMR ($CDCl_3$): ^1H, δ 2.96 [m, 12H, $P(OCH_2CH_2NMe_3^+I^-)$], 3.20 {s, 54H, [$P(OCH_2CH_2NMe_3^+I^-)$]}, 3.96 [m, 12H, $P(OCH_2CH_2NMe_3^+I^-)$]; ^{13}C, δ 54.5 [$P(OCH_2CH_2NMe_3^+I^-)$], 61.4 [$P(OCH_2CH_2NMe_3^+I^-)$], 66.7 [$P(OCH_2CH_2NMe_3^+I^-)$] ppm; ^{31}P, δ 18.2 ppm (s, 3P). Anal. Calcd for $C_{30}H_{84}N_9O_9P_3I_6$: C, 23.39; H, 5.45; N, 8.18. Found: C, 23.00; H, 5.80; N, 8.23.

$N_3P_3(OCH_2pyrMe^+I^-)_6 \cdot 4H_2O$ (7). Compound **7** was prepared from **3** by the same procedure described for **6**. Mp: 130 °C. IR: 3482 cm^{-1}, $\nu(H_2O)$. NMR ($CDCl_3$): ^1H, δ 4.35 (s, 18H, $pyrMe^+I^-$)], 5.54 [s, 12H, $OCH_2pyrMe^+I^-$], 8.05 (d, 12H, $pyrMe^+I^-$), 8.76 ppm (9d, 12H, $pyrMe^+I^-$); ^{13}C, δ 48.1($pyrMe^+I^-$), 66.2 ($POCH_2$), 125.1 (*o*-Ph), 145.3 (*m*-Ph), 155.2 (*p*-Ph) ppm; ^{31}P, δ 18.8 ppm (s, 3P). Anal. Calcd for $C_{42}H_{62}N_9O_{10}P_3I_6$: C, 29.52; H, 3.63. Found: C, 29.58; H, 3.76.

$N_4P_4(OCH_2CH_2CH_2NMe_3^+I^-)_8 \cdot 8H_2O$ (8). To a stirring absolute ethanol solution of **4** was added 9 mol equiv of methyl iodide, and the solution was warmed at reflux for 5 h. On cooling, the ionic product was precipitated out by adding a sufficient amount of diethyl ether to the clear solution of the reaction mixture. Compound **8**, a hygroscopic yellow solid, was filtered off and allowed to dry in a desiccator. Mp: 168 °C. IR: 3430 cm^{-1}, $\nu(H_2O)$. NMR ($CDCl_3$): ^1H, δ 1.88 (m, 16H, $CH_2CH_2CH_2NMe_3^+I^-$), 2.41 (m, 16H, $CH_2CH_2CH_2NMe_3^+I^-$), 3.32 [s, 72H, ($CH_2CH_2CH_2NMe_3^+I^-$)], 3.99 [m, 16H, ($POCH_2CH_2CH_2NMe_3^+I^-$)]; ^{13}C, δ 57.5 ($CH_2CH_2CH_2NMe_3^+I^-$), 58.8 ($CH_2CH_2CH_2NMe_3^+I^-$), 61.6 ($CH_2CH_2CH_2NMe_3^+I^-$), 66.5 ($POCH_2$) ppm; ^{31}P, δ 18.1 ppm (s, 3P). Anal. Calcd for $C_{49}H_{136}N_{12}O_{16}P_4I_8$: C, 25.69; H, 5.94; N, 7.38. Found: C, 25.11; H, 6.10; N, 7.73.

$N_3P_3[OCH_2CH_2NMe_3^+(NTf_2)^-]_5(OCH_2CH{=}CH_2)$ (9). To a stirring 5 mL aqueous solution of **5** (1.26 g, 1.00 mmol) in a 100 mL beaker was added 1.60 g (5.58 mmol) of lithium bis(trifluoromethanesulfonyl)amide ($LiNTf_2$) dissolved in 3 mL of water. The mixture was warmed at 40 °C for 1 h. During this time, **9** separated out as a water-insoluble, very viscous light yellow liquid. The aqueous phase was decanted off, and **9** was washed several times with fresh 5 mL quantities of water. The oily product was dissolved in acetone and evaporated in a flask under vacuum at 40 °C. NMR ($CDCl_3$): ^1H, δ 2.42 [m, 10H, ($CH_2CH_2NMe_3^+NTf_2^-$)], 3.25 [s, 45H, $P(OCH_2CH_2NMe_3^+NTf_2^-)$], 3.96 {m, 10H, [$P(OCH_2CH_2NMe_3^+NTf_2^-)$]}, 4.10 (d, 2H, $OCH_2CH{=}CH_2$), 5.15 (dd, 1H, $OCH_2CH{=}CH_2$), 6.00 ppm (dd, 2H, $OCH_2CH{=}CH_2$); ^{13}C, δ 57.8 [$P(OCH_2CH_2NMe_3^+NTf_2^-)$], 63.6 [$P(OCH_2CH_2NMe_3^+NTf_2^-)$], 67.4 [$P(OCH_2CH_2NMe_3^+NTf_2^-)$], 122.4 [q, $J_{C-F} = 23$ Hz, $NTf_2^- = CF_3SO_2)_2N^-$] ppm; ^{31}P, δ 7.0 (t, $J_{P-P} = 66$ Hz, 1P), 19.1 ppm (d, $J_{P-P} = 66$ Hz, 2P); ^{31}P, δ 18.2 ppm (s, 3P). Anal. Calcd for $C_{38}H_{70}N_{13}O_{26}P_3S_{10}F_{30}$: C, 21.54; H, 3.32; N, 8.64. Found: C, 21.49; H, 4.08; N, 8.80.

$N_3P_3[OCH_2CH_2NMe_3^+(NTf_2)^-]_6$ (10). Compound **10** was prepared from **6** and $LiNTf_2$ as for **9**. NMR ($CDCl_3$): ^1H, δ 2.21 (m, 12H, $CH_2CH_2NMe_3^+NTf_2^-$), 3.22 [s, 54H, $P(OCH_2CH_2NMe_3^+NTf_2^-)$], 3.94 [m, 12H, $P(OCH_2CH_2NMe_3^+NTf_2^-)$]; ^{13}C, δ 56.8 [$P(OCH_2CH_2NMe_3^+NTf_2^-$], 62.5 [$P(OCH_2CH_2NMe_3^+NTf_2^-$], 66.8 [$P(OCH_2CH_2NMe_3^+NTf_2^-$], 121.6 [q, $J_{C-F} = 23$ Hz, $NTf_2^- = CF_3SO_2)_2N^-$] ppm; ^{19}F, δ −78.3 ppm (s, 6F); ^{31}P, δ 18.0 ppm (s, 3P). Anal. Calcd for $C_{42}H_{78}N_{15}O_{30}P_3S_{12}F_{36}$: C, 20.72; H, 3.23; N, 8.63. Found: C, 20.55; H, 3.52; N, 8.62.

$N_3P_3[OCH_2pyrMe^+(NTf_2)^-]_6$ (11). Compound **11** was prepared from **7** and $LiNTf_2$ as described for **9**. NMR ($CDCl_3$): ^1H, δ 4.30 (s, 18H, $pyrMe^+(NTf_2)^-$)], 5.38 [s, 12H, $OCH_2pyrMe^+(NTf_2)^-$], 7.95 (d, 12H, $pyrMe^+(NTf_2)^-$), 8.62 ppm (9d, 12H, $pyrMe^+(NTf_2)^-$); ^{13}C, δ 49.0 ($pryMe^+(NTf_2)^-$), 66.2 ($POCH_2$), 119.5 [q, $J_{C-F} = 23$ Hz, $NTf_2^- = CF_3SO_2)N^-$], 125.6 (*m*-Pyr), 146.0 (*o*-Pyr), 156.0 (*p*-Pyr) ppm; ^{19}F, δ −80.1 ppm [s, 36F, $NTf_2^- = CF_3SO_2)_2N^-$]; ^{31}P, δ 17.9 ppm (s, 3P). Anal. Calcd for $C_{54}H_{54}N_{15}O_{30}P_3S_{12}F_{36}$: C, 25.39; H, 2.12. Found: C, 25.20; H, 2.70.

$N_4P_4[OCH_2CH_2CH_2NMe_3^+(NTf_2)^-]_8$ (12). Compound **12** was prepared from **8** and $LiNTf_2$ as described for **9.** NMR ($CDCl_3$): ^1H, δ 1.82 (m, 16H, $CH_2CH_2CH_2NMe_3^+NTf_2^-$), 2.46 (m, 16H, $POCH_2CH_2CH_2NMe_3^+NTf_2^-$), 3.28 [m, 72H, $CH_2CH_2CH_2NMe_3^+NTf_2^-$)], 4.03 (m, 16H, $POCH_2CH_2CH_2NMe_3^+NTf_2^-$); ^{13}C, δ 57.7 ($CH_2CH_2CH_2NMe_3^+NTf_2^-$), 58.4 ($CH_2CH_2CH_2NMe_3^+NTf_2^-$), 61.8 ($CH_2CH_2CH_2NMe_3^+NTf_2^-$), 66.9 ($POCH_2$), 122.8 [q, $J_{C-F} = 23$ Hz, $NTf_2^- = CF_3SO_2)N^-$] ppm; ^{19}F, δ −79.9 ppm (s, 6F); ^{31}P, δ 18.2 ppm (s, 3P). Anal. Calcd for $C_{64}H_{120}N_{20}O_{40}P_4S_{16}F_{48}$: C, 22.82; H, 3.57; N, 8.32. Found: C, 22.03; H, 3.71; N, 8.32.

$N_3P_3[OCH_2pyrNMe^+(BF_4)^-]_6 \cdot 4H_2O$ (13). Compound **13** was prepared from **7** and potassium tetrafluoroborate by following the procedure for **9**. However, **13** was water soluble and the crude solution mixture was evaporated to dryness. The desired product was extracted with acetone. Mp: 168 °C. NMR ($CDCl_3$): ^1H, δ 4.31 (s, 18H, $Mepyr$)], 5.43 [s, 12H, $OCH_2pyrMe^+BF_4^-$], 7.94 (d, 12H, $pyrMe^+BF_4^-$), 8.70 ppm (9d, 12H, $pyrMe^+BF_4^-$); ^{13}C, δ 48.7 ($pyrMe$), 66.6 ($POCH_2$), 125.5 (*o*-Pyr), 146.0 (*m*-Pyr), 156.1(*p*-Pyr) ppm; ^{31}P, δ 17.7 ppm (s, 3P). Anal. Calcd for $C_{42}H_{62}N_9O_{10}P_3B_6F_{24}$: C, 34.24; H, 4.23. Found: C, 34.57; H, 4.25.

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