Phosphonation of Aryloxyphosphazenes

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ABSTRACT: Two methods for the addition of pendent dialkyl phosphonate units onto aryloxyphosphazenes, at both the polymeric and cyclic trimer levels, are described. Sodium organophosphites or halogenated organophosphates were used as the phosphonating agents and were allowed to react with bromomethylene- or lithio-functionalized aryloxyphosphazenes, respectively. Phosphonation of bromomethylene−phenoxy side groups proceeded with ∼100% conversion, while phosphonation via lithiophenoxy intermediates yielded 80−85% conversion. The presence of a direct phosphorus−carbon bond in all products was confirmed by ^{13}C NMR. Well-defined, cyclic trimers and polymers were obtained via both methods.

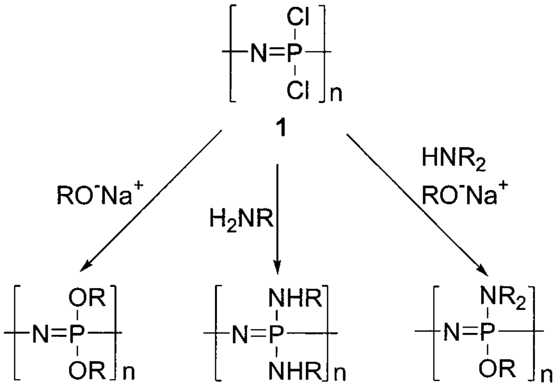
Introduction

Polyphosphazenes are a synthetically unique class of macromolecules. A wide variety of polymers are accessible through the replacement of chlorine atoms by organic units on the macromolecular precursor, poly(dichlorophosphazene) (**1**), by suitable nucleophiles as shown in Scheme 1. The synthesis of phosphazenes with pendent functional groups on the substituents, R, can be achieved through three separate pathways:[1] (1) chemical modification of the side groups, R, in a preformed polymer,[2−4] (2) treatment of poly(dichlorophosphazene) with bifunctional reagents where one of the functionalities is significantly less reactive to the phosphazene P−Cl bond,[5] or (3) treatment of poly(dichlorophosphazene) with a bifunctional reagent where one of the functional groups is protected during reaction with poly(dichlorophosphazene) and is subsequently deprotected.[1,6]

The incorporation of pendent phosphate groups onto aryloxyphosphazenes through phosphorylation (phosphorus−oxygen−carbon linkages) has been examined by us in the past.[7] However, phosphate−ester bonds are known to have limited thermal stability and are subject to chemical attack by hydroxide ions which may result in hydrolysis of the phosphorus−oxygen−carbon linkage and cleavage of the pendent phosphate group.[8] For this reason we have examined the incorporation of pendent phosphate groups into aryloxyphosphazenes attached through phosphonate (phosphorus−carbon) linkages. The use of a direct phosphorus−carbon bond ensures greater thermal and chemical stability[8,9] which should provide materials with more versatile properties.

The linkage of pendent phosphate groups to aryloxyphosphazenes is of general interest for two reasons. First, small-molecule cyclic aryloxyphosphazenes bearing pendent phosphate groups are possible fire-retardant additives for common organic polymers.[7] Second, the conversion of pendent dialkyl phosphate groups to phosphoric acid groups could lead to interesting and useful ion exchange or proton conduction membranes.

Scheme 1. Macromolecular Substitution of Poly(dichlorophosphazene) (1)



Polymers functionalized with acidic groups have been used as proton-conducting fuel cell membranes since the Gemini space mission in 1965.[10] The earliest examples for hydrogen−oxygen fuel cells were based on sulfonic acid derivatives of polystyrene. More recently, sulfonated fluorocarbon polymers such as Nafion have been used widely for hydrogen−oxygen fuel cells, but these have proved to be inadequate for direct methanol fuel cells mainly because of their high permeability to methanol.

For these reasons a severe need exists for new proton-conductive polymers. Three classes of polyphosphazenes are candidates for fuel cell applications. All bear aryloxy side groups. The first consists of polymers functionalized with carboxylic acid side groups.[6,11] The second group bears sulfonic acid groups,[2,3,12] and the third uses phosphorus-based acidic groups as functional sites.

We report here two methods for the incorporation of dialkyl phosphonate units into the side groups of aryloxyphosphazenes. In the first approach, small-molecule cyclic (**2**) and high polymeric (**3**) phosphazenes bearing bromomethylene−phenoxy side groups are treated with a sodium dialkyl phosphite as shown in Schemes 2 and 3. This method yields well-defined products at both the small-molecule and high polymeric levels. In the second route, we revisited a procedure attempted previously in our laboratory,[7] in which small-molecule cyclic (**4**) and high polymeric (**5**) phosphazenes bearing bromophenoxy side groups are treated with *n*-butyllithium followed by a dialkyl chlorophosphate as shown in Schemes 4 and 5. This method has now been improved for the synthesis of aryloxyphosphazenes with pendent dialkyl phosphonate groups and leads to well-

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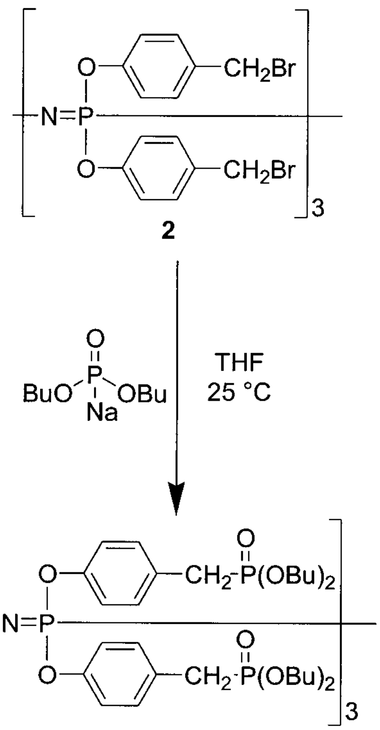
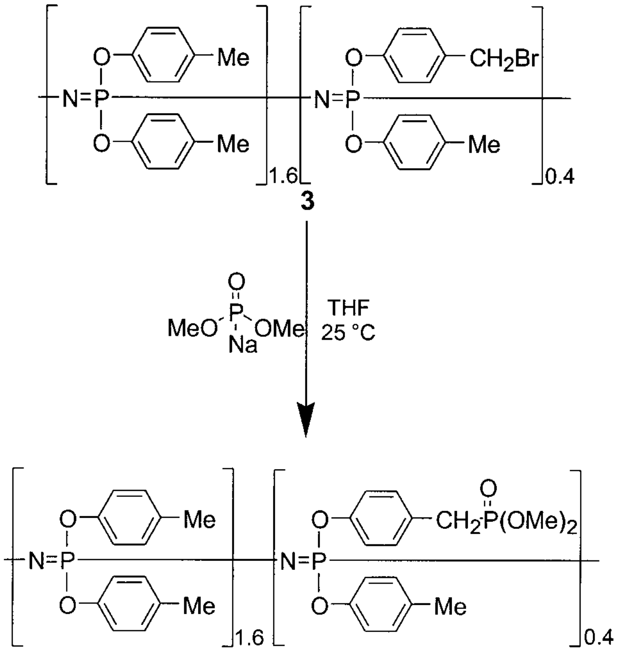
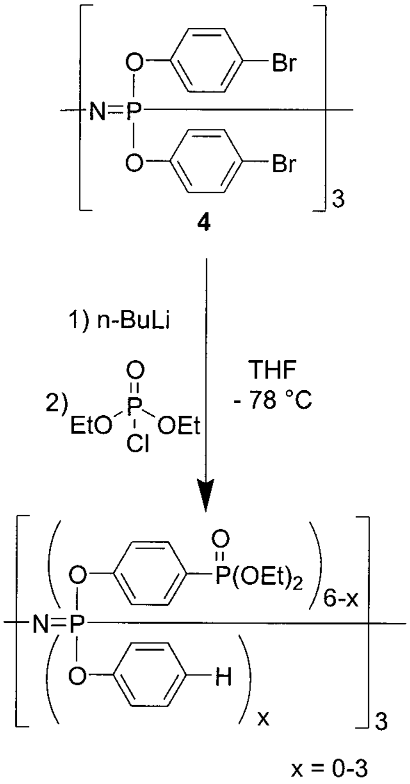
Scheme 2. Phosphonation of $N_3P_3(OC_6H_4CH_2Br)_6$ (2)



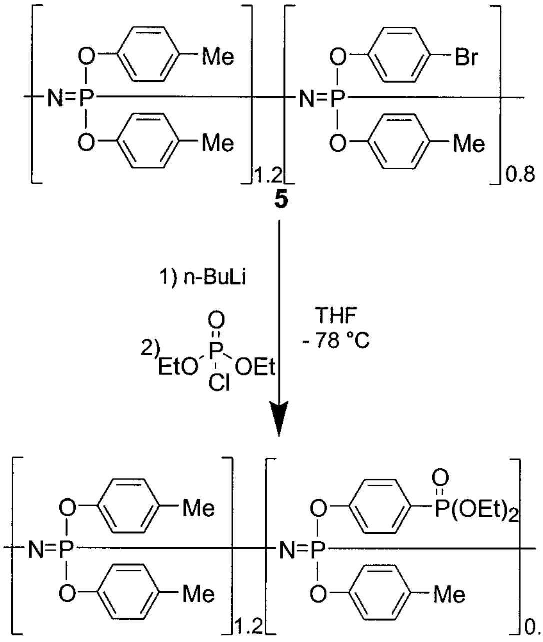
Scheme 3. Phosphonation of $[NP(OC_6H_4CH_2Br)_{0.2}(OC_6H_4CH_3)_{1.8}]_n$ (3)



Scheme 4. Phosphonation of $N_3P_3(OC_6H_4Br)_6$ (4)



Scheme 5. Phosphonation of $[NP(OC_6H_4Br)_{0.4}(OC_6H_4CH_3)_{1.6}]_n$ (5)



defined products at both the small-molecule and polymeric levels. Future studies will examine the conversion of these pendent dialkyl phosphonate groups to phosphonic acid groups as a potential route to ion exchange membranes and especially to proton-conductive fuel cell membranes.

Results and Discussion

Phosphonation of Phosphazenes Bearing Bromomethylene–Phenoxy Side Groups. The incorporation of dialkyl phosphonate units into both cyclic trimeric (**2**) and high polymeric (**3**) aryloxyphosphazenes via bromomethylene intermediates, as shown in Schemes 2 and 3, is a quantitative reaction. For **2**, a solution of hexa(4-bromomethylenephenoxy)cyclotriphosphazene[13] ($N_3P_3(OC_6H_4CH_2Br)_6$, **2**) in THF was treated with sodium dibutyl phosphite at room temperature for 16 h. Characterization by multinuclear NMR and mass spectrometry confirmed the complete conversion of the bromomethylene groups to dibutyl phosphonate groups.

Phosphonation of polymer **3** was achieved by treatment of a solution of 10% brominated poly[bis(4-methylphenoxy)phosphazene][13,14] ($[NP(OC_6H_4CH_2Br)_{0.2}(OC_6H_4CH_3)_{1.8}]_n$, **3**) in THF with sodium dimethyl phosphite at room temperature for 16 h. The final polymer was a tough, leathery material. Multinuclear NMR and elemental analysis indicated complete conversion of the bromomethylene groups to dimethyl phosphonate groups. GPC of the polymer before and after phosphonation revealed no significant change in molecular weight. DCS analysis of the phosphonated polymer revealed a glass transition temperature (T_g) of 3 °C. This is not a significant change over the T_g (2 °C) found for the parent polymer (**3**). However, polymer **3** was found to have a melting transition temperature (T_m) of 103 °C. This transition was not observed in the phosphonated polymer and was attributed to an increase in free volume.

Phosphonation of Phosphazenes via Lithiophenoxy Side Groups. One potential disadvantage of the above approach is the required bromination[13,14] and purification of hexakis(4-methylphenoxy)cyclotriphosphazene or poly[bis(4-methylphenoxy)phosphazene] before phosphonation. Thus, we have reinvestigated the use of lithiophenoxy intermediates to produce phosphonated phosphazenes. The use of lithiophenoxy intermediates as a means for the side group modification of other derivatives was studied previously at both the phosphazene cyclic trimer[15,16] and high polymer levels.[4] In the earlier studies lithiophenoxy intermediates were treated with electrophiles, such as diphenylchlorophosphine, triphenyltin chloride, and (triphenylphosphine)–gold(I) chloride, as possible carrier molecules for transition-metal catalysts. However, the extension of this approach to include phosphoryl electrophiles such as diethyl chlorophosphate and diphenyl chlorophosphate was found previously to be a complex reaction that resulted in minimal phosphonation of the cyclic trimer.[7] Similarly, the use of lithiophenoxy intermediates at the high polymer level produced insoluble products with only slight evidence of phosphonation.[7] We now report 80-85% conversions of the bromine atoms in both cyclic trimeric (**4**) and polymeric (**5**) aryloxyphosphazenes to dialkyl phosphonate groups via lithiophenoxy intermediates as shown in Schemes 4 and 5. For the cyclic trimer system **4**, a solution of hexa(4-bromophenoxy)cyclotriphosphazene[15] ($N_3P_3(OC_6H_4Br)_6$, **4**) in THF was treated with *n*-butyllithium at −78 °C, followed by the addition of diethyl chlorophosphate at −78 °C to yield the phosphonated trimer. After washing with water and hexanes, the resultant clear yellow oil was examined by multinuclear NMR and mass spectrometry. The ^{1}H and ^{31}P NMR spectra and mass spectral analysis revealed that ~82% of the bromophenoxy groups had been phosphonated.

The analogous high polymeric reaction had been attempted previously with $[NP(OC_6H_4Br)_2]_n$ as the starting polymer.[7] In an effort to obtain soluble products, we decreased the projected amount of phosphonation from 100% to 20%. However, all attempts that followed the earlier procedure failed to produce soluble materials. Insoluble products were attributed to the intermolecular cross-linking of lithiophonoxy and bromophenoxy side groups during the addition of *n*-BuLi. Interestingly, intermolecular coupling in the trimeric system **4** was not observed. It is anticipated that minimal coupling of the cyclic trimers does occur, but this should not result in insoluble materials. However, minimal amounts of intermolecular coupling, (cross-links) in polymeric systems frequently result in insoluble materials. Thus, soluble products were obtained by reversing the order of addition in the lithiation step. Thus, a solution of poly[{(4-bromophenoxy)$_{0.4}$(4-methylphenoxy)$_{1.6}$}phosphazene] ($[NP(OC_6H_4Br)_{0.4}(OC_6H_4CH_3)_{1.6}]_n$, **5**) in THF at −78 °C was added to a solution of *n*-butyllithium in THF at −78 °C, followed by the addition of diethyl chlorophosphate. After precipitations into water and cyclohexane, the resultant tough leathery material was characterized by multinuclear NMR and elemental analysis. Like the cyclic trimeric reaction, the ^{1}H and ^{31}P NMR spectra revealed that ~83% of the bromophenoxy groups had been phosphonated. The molecular weight (M_n = 270 000, PDI = 1.5) of the phosphonated polymer estimated by GPC was about half that of the parent polymer (**5**, M_n = 520 000, PDI = 1.3). This has been attributed to backbone cleavage by *n*-butyllithium. DCS analysis of the phosphonated polymer revealed a glass transition temperature (T_g) of −5 °C. This is ~10 °C lower than the T_g (4 °C) found for the parent polymer (**3**). Moreover, polymer **3** was found to have a melting transition temperature (T_m) of 136 °C. This transition was not observed in the phosphonated polymer. Both the decrease in T_g and the absence of a melting transition in the phosphonated polymer were attributed to an increase in free volume.

Confirmation of Phosphorus–Carbon Linkage by ^{13}C NMR. Figure 1 shows the ^{13}C NMR spectrum of the product obtained by the treatment of **2** with sodium dibutyl phosphite as shown in Scheme 2. Confirmation of the phosphorus–carbon bond was found from the large ^1J coupling (138.2 Hz) in the doublet of carbon **e** at 33.1 ppm (Figure 1, inset) and the small ^2J coupling of carbons **f** (66.3 ppm, $^2J_{C-P}$ = 7.2 Hz) and **d** (129.3 ppm, $^2J_{C-P}$ = 9.0 Hz). In addition, ^3J coupling was also found for carbons **g** (33.0 ppm, $^3J_{C-P}$ = 6.3 Hz) and **c** (131.3 ppm, $^3J_{C-P}$ = 6.3 Hz). For the phosphonation of **3** with sodium dimethyl phosphite (Scheme 3), long-range coupling was lost due to the decreased resolution that is typical of many polymeric systems. However, the ^1J coupling of the benzyl carbon (analogous to carbon **e** above) was still evident in the doublet at 32.8 ppm ($^1J_{C-P}$ = 138 Hz).

Similar evidence for direct phosphorus–carbon bond formation was found in the ^{13}C NMR spectra of the products obtained by phosphonation via lithiophenoxy intermediates. Phosphonation of **4** (Scheme 4) gave rise to a doublet at 127.2 ppm for the para-aryl carbon bonded directly to the phosphorus atom with a large ^1J coupling (191.2 Hz). Longer-range ^2J and ^3J couplings were also consistent with direct phosphorus–carbon bond formation. For the phosphonation of **5** (Scheme 5), most long-range coupling was again obscured; however, the large ^1J coupling of the para-aryl carbon to the phosphorus atom was still evident in the doublet at 125.2 ppm ($^1J_{C-P}$ = 190 Hz).

Efficiency of Phosphonation Reactions. The overall efficiency of the two phosphonation methods with respect to percent conversion of the initial bromine atoms present was determined by ^{31}P NMR and mass spectral analysis of the model cyclic trimers **2** and **4**. ^{31}P NMR and elemental analysis were used for the high polymers **3** and **5**. The phosphonation of **2** proceeded with 100% conversion. This was evident from the observed 2:1 integration of the dialkyl phosphonate phosphorus resonance (26.3 ppm) to the phosphazene phosphorus resonance (9.3 ppm) found in the ^{31}P NMR spectrum. Moreover, MALDI-mass spectral data indicated only the mass of the hexasubstituted trimer (*m*/*z* 1932 MH$^+$, *m*/*z* 1954 MNa$^+$). A similar argument was

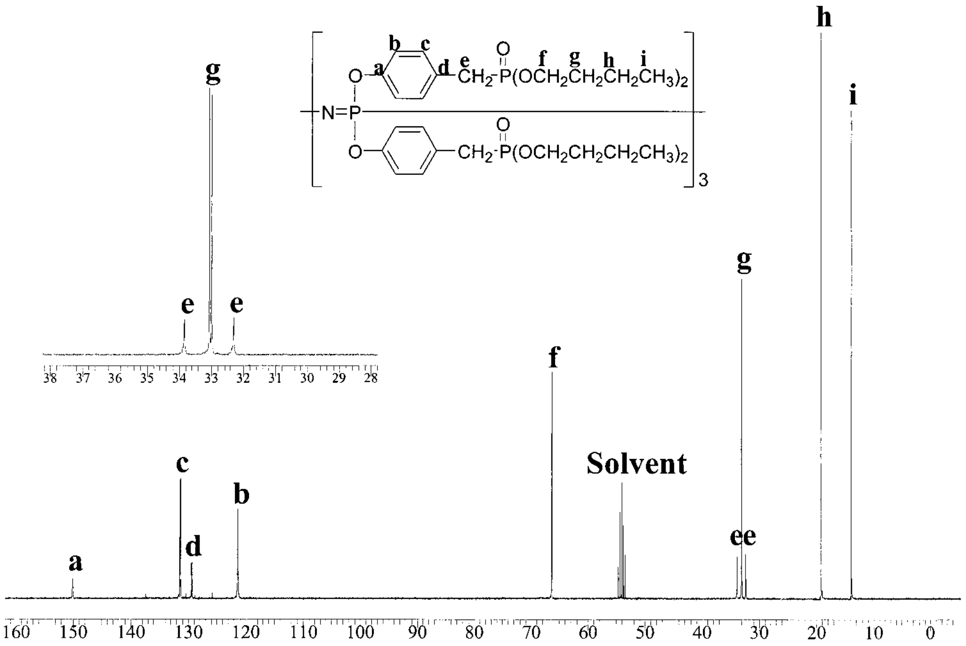


Figure 1. ^{13}C NMR spectrum of the product obtained via phosphonation of **2**.

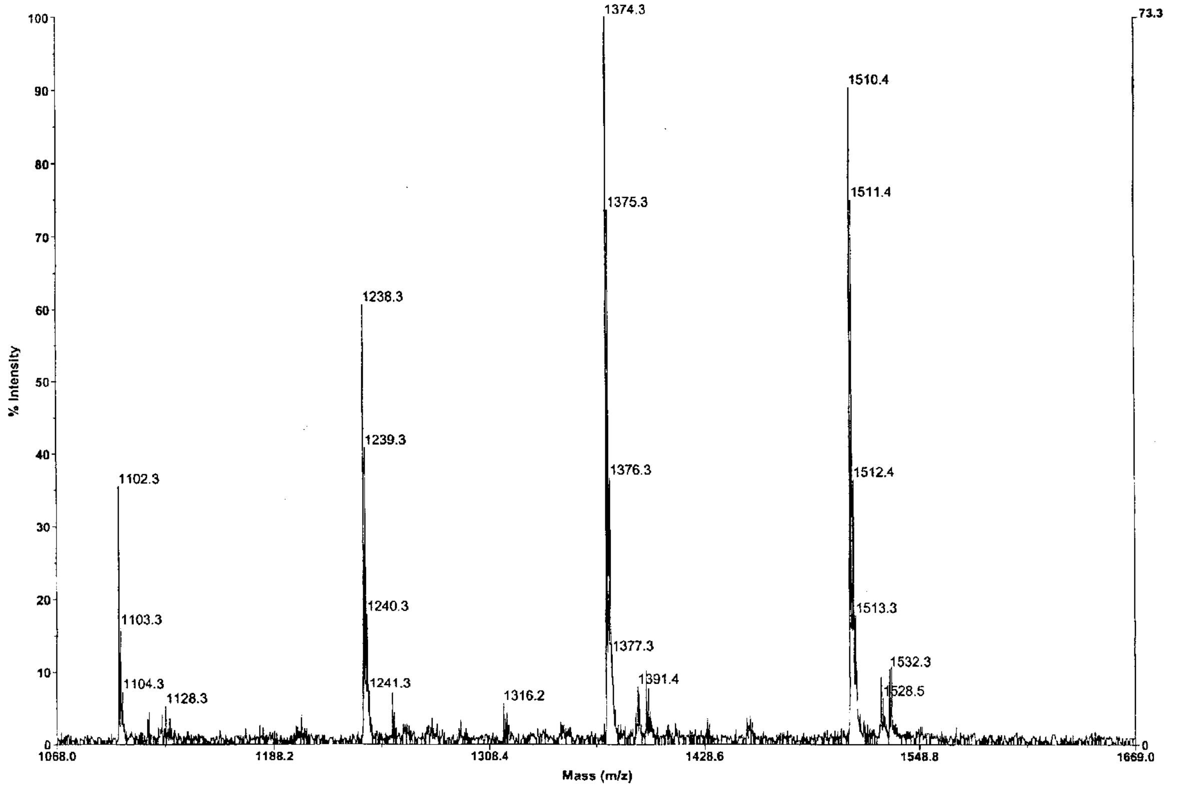


Figure 2. APCI mass spectrum of the product obtained via phosphonation of **4**.

made for the phosphonation of **3**. Here the integration of the dialkyl phosphonate phosphorus resonance (27.4 ppm) to the phosphazene phosphorus resonance (−18.4 ppm) found in the ^{31}P NMR spectrum was 0.2:1, indicating that ~100% of the bromomethylene-functionalized side groups had been phosphonated. Elemental analysis, which was within experimental error, confirmed the ^{31}P NMR data.

Phosphonation via lithiophenoxy intermediates proceeded with 80−85% conversion of the bromophenoxy side groups to dialkyl phosphonate side groups. For the phosphonation of **4**, the ^{31}P NMR spectrum revealed multiple peaks between 17.4 and 17.9 ppm indicative of the dialkyl phosphonate phosphorus and between 7.7 and 7.9 ppm for the phosphazene phosphorus. Integration revealed a 1.64:1 ratio of the dialkyl phosphonate phosphorus resonances to the phosphazene phosphorus resonances, which indicated 82% phosphonation. In addition, APCI-mass spectral data (Figure 2) indicated the product was a mixture with masses *m/z* 1102 MH$^+$ (triphosphonate, 3.0%), 1238 MH$^+$ (tetraphosphonate, 12.0%), 1374 MH$^+$ (pentaphosphonate, 32.3%), and 1510 MH$^+$ (hexaphosphonate, 37.2%). Interestingly, the masses found revealed that, for the remaining ~18% of

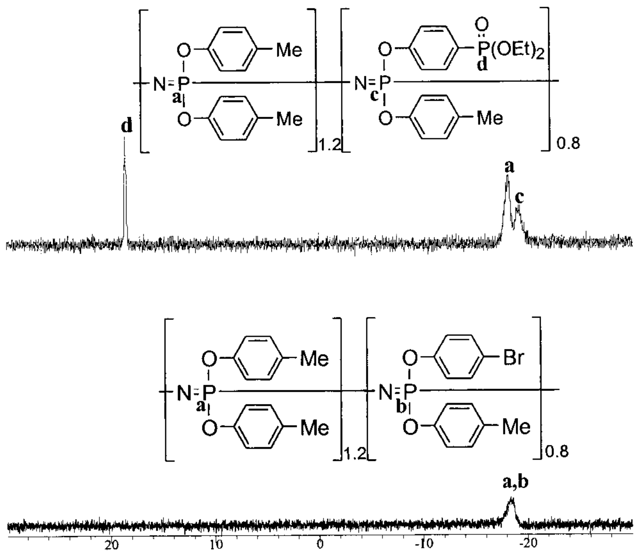


Figure 3. ^{31}P NMR spectrum of the product obtained via phosphonation of **5**.

the initial bromophenoxy groups that did not undergo phosphonation, essentially all of the bromine atoms had been replaced by hydrogen. Thus, rather than incomplete lithiation, the limiting factor in the overall reaction appears to be side reactions of the highly reactive lithiophenoxy intermediate, which may occur during the addition of diethyl chlorophosphate.

Figure 3 shows the ^{31}P NMR spectra of **5** and the product obtained after phosphonation as shown in Scheme 5. Polymer **5** shows a broad resonance attributed to the overlapping signals of phosphorus atoms **a** and **b**. The spectrum of the phosphonated product displays three distinct resonances: 18.7 ppm (dialkyl phosphonate phosphorus, **d**) and −18.1 and −18.9 ppm (phosphazene phosphorus atoms, **a** and **c**). The integration of **d** to **a** and **c** was 0.34:1, indicating that 83% of the bromophenoxy side groups had been phosphonated. Elemental analysis showed significantly less bromine in the product than calculated if the remaining 17% of the bromophenoxy groups had not been lithiated. This again confirmed that the limiting factor in the phosphonation is side reactions of the lithiophenoxy intermediate that may occur during the addition of diethyl chlorophosphate.

Interaction of $[NP(OC_6H_4Br)_{0.4}(OC_6H_4CH_3)_{1.6}]_n$ with *n*-Butyllithium. As mentioned previously, the synthesis of soluble phosphonated polymers via lithiophenoxy intermediates was only achieved when a solution of **5** in THF at −78 °C was added to a solution of *n*-butyllithium in THF at −78 °C followed by addition of diethyl chlorophosphate. The reverse process, in which the *n*-butyllithium was added to a solution of the polymer, resulted only in insoluble cross-linked materials. Three possible mechanisms have been proposed for the cross-linking of lithiophenoxy polymers.[4] First, intermolecular coupling could take place between lithiophenoxy and bromophenoxy side groups. Second, the interaction of bromophenoxy side groups with *n*-butyllithium could give rise to benzyne formation and subsequent intermolecular coupling with lithiophenoxy or other benzyne side groups. Third, lithiophenoxy side groups could interact with a phosphorus atom in the phosphazene backbone, leading to displacement of an aryloxy side group and intermolecular coupling.

Previously, the third mechanism had been favored on the grounds that phenyllithium will displace phenoxy side groups from the cyclic trimer, $N_3P_3(OC_6H_5)_6$, at normal temperatures.[4,17] However, on the basis of the new results, we propose that the first mechanism is the most plausible. The order of addition in the lithiation step should not affect benzyne formation or their possible coupling reactions, as proposed in the second mechanism. Similarly, displacement of aryloxy side groups from the backbone phosphorus atoms should also be unaffected by the order of addition. The first mechanism is thus the most likely. In the case where *n*-butyllithium is added to a solution of the polymer, there are significant opportunities for the reaction of lithiophenoxy and bromophenoxy substituents. However, in the case where the polymer is added to a solution of *n*-butyllithium, this opportunity is significantly reduced.

Conclusions

In this study, we examined two different routes to the phosphonation of aryloxyphosphazenes. Phosphonation via bromomethylene-functionalized aryloxyphosphazenes proceeded with 100% conversion, while phosphonation via lithiophenoxy intermediates resulted in 80−85% conversion. In addition, both of these methods have been demonstrated on small-molecule model cyclic species as well as high polymeric aryloxyphosphazenes. The formation of a direct phosphorus−carbon bond in all products was confirmed by ^{13}C NMR spectroscopy. The cyclic compounds discussed are currently being investigated as fire-retardant additives in common organic polymers. Ongoing studies with the polymeric compounds will examine the upper limit of phosphonation, the variety of phosphoryl electrophiles suitable for these two methods and possible routes for the conversion of these pendent phosphonate groups to phosphonic acid groups. Initial results have shown that polyphosphazenes bearing diphenyl phosphonate groups (obtained through the reaction of diphenyl chlorophosphate with polymeric lithiophenoxy aryloxyphosphazenes) are quite easily converted to the corresponding monoacid/monoester by basic hydrolysis and subsequent acidification. A detailed discussion of this work will be presented in a future publication. It is anticipated that aryloxyphosphazenes bearing phosphonic acid groups will be good candidates for ion-exchange membrane applications, particularly in proton conduction membranes for use in fuel cells.

Experimental Section

Materials. Dimethyl phosphite, 98%; dibutyl phosphite, 96%; diethyl chlorophosphate, 97%; *n*-butyllithium (1.6 M in hexanes), 4-methylphenol, 99%; 4-bromophenol, 99%; tetra(*n*-butyl)ammonium bromide, 99%; *N*-bromosuccinimide, 99%; and benzoyl peroxide, 97%; were obtained from Aldrich and used as received. Sodium hydride (Fluka, 60% suspension in mineral oil) (Aldrich, 95%) was used as received. Tetrahydrofuran (THF) was obtained from EM Science and distilled from sodium benzophenone ketyl prior to use. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical Co.) was recrystallized from heptane and sublimed at 40 °C (0.05 mmHg). Poly(dichlorophosphazene) (**1**) was obtained by ring-opening polymerization of hexachlorocyclotriphosphazene.[18,19] $N_3P_3(OC_6H_4CH_2Br)_6$ (**2**) and $N_3P_3(OC_6H_4Br)_6$ (**4**) were synthesized according to previously published procedures.[13,14] All reactions were carried out under an atmosphere of dry argon.

Equipment. High-field ^{1}H (360 MHz), ^{13}C (90 MHz), and ^{31}P (146 MHz) NMR spectra were obtained using a Bruker

AMX-360 spectrometer; ^{13}C (126 MHz) spectra for the polymeric samples were obtained using a Bruker AMX-500 spectrometer. The ^{31}P and^{13}C spectra were proton decoupled. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield from the reference. ^{1}H and ^{13}C were referenced to external tetramethylsilane. All NMR spectra were obtained in d_8-THF unless otherwise noted with chemical shifts recorded in ppm and coupling constants recorded in hertz. Molecular weights were estimated using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1047A refractive index detector. The samples were eluted with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate in THF. The GPC system was calibrated with polystyrene standards (Polysciences). Elemental analyses were performed by Quantitative Technologies of Whitehouse, NJ. MALDI-mass spectral data were obtained using a Voyager DE STR spectrometer in positive ion mode. APCI-mass spectral data were obtained using a Mariner spectrometer, also in positive ion mode. DSC measurements were carried out using a Perkin-Elmer-7 thermal analysis system equipped with a PC computer. Glass and melting transition temperatures were obtained by heating the polymer samples from −50 to 200 °C at a rate of 10 °C/min, under an atmosphere of dry nitrogen. Calibration was preformed using cyclohexane.

Preparation of $[NP(OC_6H_4CH_3)_2]_n$. This procedure was modified from a previous literature procedure.[13] 4-Methylphenol (61.8 g, 0.572 mol) was dissolved in 250 mL of THF and added dropwise to a suspension of sodium hydride (21.8 g, 0.545 mol) and tetra(*n*-butyl)ammonium bromide (1.0 g, 3.0 mmol) in 200 mL of THF. The resultant sodium aryloxide was added dropwise to a stirring solution of poly(dichlorophosphazene) (**1**) (15.0 g, 0.129 mol in 900 mL of THF) in an autoclave. The autoclave was pressurized to 1 atm with argon, sealed, and heated to 150 °C. After 12 h the autoclave was cooled to room temperature and the contents precipitated into 15 L of acidified H_2O (30 mL of concentrated HCl). The polymer was reprecipitated from THF four times into 95% ethanol (1 time), H_2O (1 time), and hexanes (2 times). The desired product was dried at <0.1 mmHg for 24 h at room temperature (RT) to yield a white solid (27 g, 81% yield). ^{1}H NMR: δ 2.1 (s, 3H, $-\mathrm{Ar}\mathit{CH}_3$), δ 6.5 (d, 2H, $^{3}J_{\mathrm{H-H}} = 8.2$, $-\mathrm{O}\mathit{ArCH}_3$), and δ 6.8 (d, 2H, $^{3}J_{\mathrm{H-H}} = 8.2$, $-\mathit{OAr}\mathrm{CH}_3$). ^{31}P NMR: δ −18.5 (br, $-\mathit{P}{=}\mathit{N}-$). $M_{\mathrm{n}} = 370\,000$; PDI = 1.4.

Preparation of $[NP(OC_6H_4CH_2Br)_{0.2}(OC_6H_4CH_3)_{1.8}]_n$ (3). This procedure was modified from a previous literature procedure.[13,14] $[NP(OC_6H_4CH_3)_2]_n$ (5.0 g, 19 mmol) was dissolved in 800 mL of carbon tetrachloride. *N*-Bromosuccinimide (0.77 g, 4.3 mmol) and benzoyl peroxide (0.05 g, 0.2 mmol) were added. The solution was shielded from light and brought rapidly to reflux for 3 h. The solution was cooled, filtered, concentrated under reduced pressure, and precipitated into hexanes. The polymer was reprecipitated from THF into hexanes two additional times. The desired product was dried at <0.1 mmHg for 24 h at RT to yield a tan solid (4.4 g, 84% yield). ^{1}H NMR: δ 2.1 (s, 3H × 0.9, $-\mathrm{Ar}\mathit{CH}_3$), δ 4.3 (s, 2H × 0.1, $-\mathrm{Ar}\mathit{CH}_2\mathrm{Br}$), and δ 6.5−6.9 (multiple, 4H, $-\mathrm{O}\mathit{Ar}\mathrm{CH}_3$ and $-\mathrm{O}\mathit{Ar}\mathrm{CH}_2\mathrm{Br}$). ^{31}P NMR: δ −18.4 (br, $-\mathit{P}{=}\mathit{N}-$). Elemental analysis: found (calculated): C, 60.01 (61.13); H, 4.89 (5.07); P, 11.75 (11.25); N, 4.96 (5.09); Br, 6.43 (5.81); Cl, 0.62 (0.00). $M_{\mathrm{n}} = 340\,000$; PDI = 1.5.

Preparation of $[NP(OC_6H_4Br)_{0.4}(OC_6H_4CH_3)_{1.6}]_n$ (5). 4-Bromophenol (11.9 g, 69.0 mmol) was dissolved in 50 mL of THF and added dropwise to a suspension of sodium hydride (2.76 g, 69.0 mmol) in 50 mL of THF. The resultant sodium aryloxide was added dropwise to the stirring solution of poly(dichlorophosphazene) (**1**) (20.0 g, 0.172 mol in 700 mL of THF) in an autoclave and stirred for 30 min. 4-Methylphenol (74.5 g, 0.690 mol) was dissolved in 200 mL of THF and added dropwise to a suspension of sodium hydride (26.2 g, 0.656 mol) and tetra(*n*-butyl)ammonium bromide (1.0 g, 3.0 mmol) in 300 mL of THF. The resultant sodium aryloxide was added dropwise to the autoclave. The autoclave was pressurized to 1 atm with argon, sealed, and heated to 150 °C. After 26 h the autoclave was cooled to room temperature, and the contents precipitated into 15 L of acidified H_2O (30 mL of concentrated HCl). The polymer was reprecipitated from THF four times into 95% ethanol (1 time), H_2O (1 time), and hexanes (2 times). Prior to the last precipitation the polymer solution in THF was vacuum-filtered. The desired product was dried at <0.1 mmHg for 24 h at RT to yield a white solid (34 g, 69% yield). ^{1}H NMR: δ 2.1 (s, 3H × 0.8, $-\mathrm{Ar}\mathit{CH}_3$) and δ 6.5−7.0 (multiple, 4H, $-\mathrm{O}\mathit{Ar}\mathrm{Br}$ and $-\mathrm{O}\mathit{Ar}\mathrm{CH}_3$). ^{31}P NMR: δ −18.2 (br, $-\mathit{P}{=}\mathit{N}-$). Elemental analysis: found (calculated): C, 56.20 (57.27); H, 4.23 (4.53); P, 11.39 (10.86); N, 4.79 (4.91); Br, 11.35 (11.21); Cl, 762 ppm (0.00). $M_{\mathrm{n}} = 520\,000$; PDI = 1.3.

Phosphonation of $N_3P_3(OC_6H_4CH_2Br)_6$. Dibutyl phosphite (3.88 g, 20.0 mmol) was added dropwise to a suspension of sodium hydride (0.46 g, 19 mmol) in 50 mL of THF and stirred at 40 °C for 16 h. The sodium dibutyl phosphite solution was then added dropwise to a solution of **2** (2.0 g, 1.6 mmol in 400 mL of THF) and stirred for 16 h at RT. The solvent was removed by reduced pressure rotary evaporation, and the resultant residue was treated with 500 mL of H_2O (2 times) and 500 mL of hexanes (2 times). The product was dissolved in 25 mL of THF and filtered. The THF was removed by reduced pressure rotary evaporation. The desired product was dried at <0.1 mmHg for 24 h at RT to yield a clear yellow oil (2.05 g, 66% yield). ^{1}H NMR (d_2-CH_2Cl_2): δ 1.1 (t, 6H, $^{3}J_{\mathrm{H-H}} = 7.3$, $-\mathrm{OCH_2CH_2CH_2}\mathit{CH}_3$), δ 1.6 (sextet, 4H, $^{3}J_{\mathrm{H-H}} = 7.7$, $-\mathrm{OCH_2CH_2}\mathit{CH}_2\mathrm{CH_3}$), δ 1.8 (m, 4H, $-\mathrm{OCH_2}\mathit{CH}_2\mathrm{CH_2CH_3}$), δ 3.3 (d, 2H, $^{2}J_{\mathrm{H-P}} = 21.9$, $-\mathrm{Ar}\mathit{CH}_2\mathrm{P}-$), δ 4.1 (m, 4H, $-\mathrm{O}\mathit{CH}_2\text{-}\mathrm{CH_2CH_2CH_3}$,), δ 7.1 (d, 2H, $^{3}J_{\mathrm{H-H}} = 8.7$, $-\mathit{OAr}\mathrm{CH_2P}$), and 7.4 (dd, 2H, $^{3}J_{\mathrm{H-H}} = 8.7$, $^{4}J_{\mathrm{H-P}} = 2.3$, $-\mathrm{O}\mathit{ArCH}_2\mathrm{P}-$). ^{13}C NMR ($d_2$-$CH_2Cl_2$): δ 13.8 (s, $-\mathrm{OCH_2CH_2CH_2}\mathit{CH}_3$), δ 19.2 (s, $-\mathrm{OCH_2}\text{-}\mathrm{CH_2}\mathit{CH}_2\mathrm{CH_3}$), δ 33.0 (d, $^{3}J_{\mathrm{C-P}} = 6.3$, $-\mathrm{OCH_2}\mathit{CH}_2\mathrm{CH_2CH_3}$), δ 33.1 (d, $^{1}J_{\mathrm{C-P}} = 138.2$, $-\mathrm{Ar}\mathit{CH}_2\mathrm{P}-$), δ 66.3 (d, $^{2}J_{\mathrm{C-P}} = 7.2$, $-\mathrm{O}\mathit{CH}_2\mathrm{CH_2CH_2CH_3}$), δ 121.3 (s, $-\mathrm{O}\mathit{Ar}\mathrm{CH_2P}-$), δ 129.3 (d, $^{2}J_{\mathrm{C-P}} = 9.0$, $-\mathrm{O}\mathit{ArCH}_2\mathrm{P}-$), δ 131.3 (d, $^{3}J_{\mathrm{C-P}} = 6.3$, $-\mathrm{O}\mathit{Ar}\mathrm{CH_2}\text{-}\mathrm{P}-$), δ 150.0 (s, $-\mathit{OAr}\mathrm{CH_2P}-$). ^{31}P NMR ($d_2$-$CH_2Cl_2$): δ 9.3 (s, 3P, $-\mathit{P}(\mathrm{OArCH_2P}-)_2{=}\mathit{N}-$) and 26.3 (s, 6P, $-\mathrm{ArCH_2}\mathit{P}-$). MALDI-MS: *m*/*z* 1932 MH^+ base peak.

Phosphonation of $[NP(OC_6H_4CH_2Br)_{0.2}(OC_6H_4CH_3)_{1.8}]_n$. Dimethyl phosphite (1.0 g, 9.0 mmol) was added dropwise to a suspension of sodium hydride (0.36 g, 9.0 mmol) in 30 mL of THF and stirred at room temperature until clear. The sodium dimethyl phosphite solution was then added to a solution of **3** (4.2 g, 15 mmol in 800 mL of THF) via syringe and let to stir at room temperature over 16 h. The solution was concentrated to 100 mL by reduced pressure rotary evaporation, and the polymer precipitated into methanol. At this point the polymer did not dissolve in THF and thus was reprecipitated from toluene into hexanes. The desired product was dried at <0.1 mmHg for 24 h at RT to yield a tan solid (4.0 g, 94% yield). ^{1}H NMR (d_8-toleune): δ 2.2 (s, 3H × 0.9, $-\mathrm{Ar}\mathit{CH}_3$), δ 2.9 (br, 2H × 0.1, $-\mathrm{Ar}\mathit{CH}_2\mathrm{P}-$), δ 3.4 (br, 6H × 0.1, $-\mathrm{O}\mathit{CH}_3$) and δ 6.7−7.5 (m, 4H, $-\mathrm{O}\mathit{Ar}\mathrm{CH_2P}-$ and $-\mathrm{O}\mathit{Ar}\mathrm{CH_3}$). ^{13}C NMR ($d_8$-toluene): δ 20.9 (s, $\mathrm{Ar}\mathit{CH}_3$), δ 32.8 (d, $^{1}J_{\mathrm{C-P}} = 138$, $-\mathrm{Ar}\mathit{CH}_2\text{-}\mathrm{P}-$), δ 52.6 (br, $-\mathrm{O}\mathit{CH}_3$), δ 122.1 (s, $-\mathrm{O}\mathit{Ar}\mathrm{CH_3}$), δ 122.3 (s, $-\mathrm{O}\mathit{Ar}\mathrm{CH_2P}-$), δ 130.1 (s, $-\mathrm{O}\mathit{Ar}\mathrm{CH_3}$), δ 131.1 (brs, $-\mathrm{O}\mathit{Ar}\mathrm{CH_2}\text{-}\mathrm{P}-$), δ 133.2 (brs, $-\mathrm{O}\mathit{Ar}\mathrm{CH_3}$), δ 150.7 (s, $-\mathit{OAr}\mathrm{CH_3}$), δ 151.8 (brs, $-\mathit{OAr}\mathrm{CH_2P}-$), $-\mathrm{O}\mathit{ArCH}_2\mathrm{P}-$ resonance not observed presumably due to solvent overlap. ^{31}P NMR (d_8-toluene): δ −18.4 (br, 1P, $-\mathit{P}(\mathrm{OArCH_3})(\mathrm{OArCH_2P}-){=}\mathit{N}-$) and δ 27.4 (br, 1P × 0.2, $\mathrm{ArCH_2}\mathit{P}-$). Elemental analysis, found (calculated): C, 60.48 (61.58); H, 5.12 (5.39); P, 12.25 (13.23); N, 4.86 (4.99); Br, 0.13 (0.00); Cl, 0.55 (0.00). $M_{\mathrm{n}} = 370\,000$; PDI = 1.5 (sample prepared by dissolving in toluene and diluting 10 times with THF).

Phosphonation of $N_3P_3(OC_6H_4Br)_6$. Compound **4** (2 g, 1.71 mmol) was dissolved in 400 mL of THF and cooled to −78 °C. To this was added *n*-butyllithium (8.35 mL, 13.4 mmol). The reaction stirred for 1 h at −78 °C, at which time diethyl chlorophosphate (6.94 g, 40.2 mmol) was added dropwise. The reaction was held at −78 °C for an additional 2 h and then allowed to warm to room temperature overnight. The solvent was removed by reduced pressure rotary evaporation, and the resultant residue was treated with 500 mL of H_2O (2 times) and 500 mL of hexanes (2 times). The desired product was dried at <0.1 mmHg for 24 h at RT to yield a yellow oil (1.74 g, 67% yield). ^{1}H NMR (d_2-$\mathrm{CH_2Cl_2}$): δ 1.2 (t, 6H × 0.82, $^{3}J_{\mathrm{H-H}} = 7.1$, $-\mathrm{OCH_2}\mathit{CH_3}$), δ 4.0 (m, 4H × 0.82, $-\mathrm{O}\mathit{CH_2}\mathrm{CH_3}$) and δ 6.6−7.7 (multiple, 4H × 0.82 + 5H × 0.18, $-\mathrm{O}\mathit{Ar}$ and $-\mathrm{O}\mathit{Ar}\mathrm{P}-$). ^{13}C NMR ($d_2$-$\mathrm{CH_2Cl_2}$): δ 16.9 (d, $^{3}J_{\mathrm{C-P}} = 5.4$, $-\mathrm{OCH_2}\mathit{CH_3}$), δ 62.8−63.1 (multiple d, $^{2}J_{\mathrm{C-P}} = 5.4$, $-\mathrm{O}\mathit{CH_2}$-$\mathrm{CH_3}$), δ 121.7 (d, $^{3}J_{\mathrm{C-P}} = 17.1$, $-\mathrm{O}\mathit{Ar}\mathrm{P}-$), δ 126.4 (s, $-\mathrm{O}\mathit{Ar}$), δ 127.2 (d, $^{1}J_{\mathrm{C-P}} = 191.2$, $-\mathrm{O}\mathit{ArP}-$), δ 130.4−130.6 (multiple s, $-\mathrm{O}\mathit{Ar}$), δ 130.2−134.5 (multiple d, $^{2}J_{\mathrm{C-P}} = 11.7$, $-\mathrm{O}\mathit{Ar}\mathrm{P}-$), δ 150.8 (s, $-\mathit{OAr}$), δ 154.1 (bs, $-\mathit{OAr}\mathrm{P}-$), second $-\mathrm{O}\mathit{Ar}$ resonance not observed presumably due to overlap with doublet at δ 121.7. ^{31}P NMR (d_2-$\mathrm{CH_2Cl_2}$): δ 7.7−8.9 (multiple, 3P, $-\mathit{P}{=}\mathit{N}-$), 17.4−17.9 (multiple, 6P × 0.82, $-\mathrm{Ar}\mathit{P}-$). APCI−MS: *m*/*z* 1102 (triphosphonate, 3.0%), 1238 (tetraphosphonate, 12.0%), 1374 (pentaphosphonate, 32.3%), and 1510 (hexaphosphonate, 37.2%) MH^{+} base peaks.

Phosphonation of $[\mathrm{NP(OC_6H_4Br)_{0.4}(OC_6H_4CH_3)_{1.6}}]_n$. *n*-Butyllithium (16.0 mL, 25.6 mmol) was added dropwise to 500 mL of THF at − 78 °C. Compound **5** (1.0 g, 3.5 mmol) was dissolved in 300 mL of THF, cooled to −78 °C, and added to the butyllithium solution via cannula. After holding at −78 °C for 1 h, diethyl chlorophosphate (9.31 g, 54.0 mmol) was added dropwise. The reaction was held at −78 °C for an additional 3 h and then allowed to warm to room temperature overnight. The reaction mass was filtered and the solution concentrated to 50 mL by reduced pressure rotary evaporation, and the product was then precipitated into water. The polymer was reprecipitated from THF 2 times into water (1 time) and cyclohexane (1 time). The desired product was dried at <0.1 mmHg for 24 h at RT to yield a white solid (0.83 g, 77% yield). ^{1}H NMR: δ 1.2 (t, 6H × 0.16, $^{3}J_{\mathrm{H-H}} = 6.9$, $-\mathrm{OCH_2}\mathit{CH_3}$), δ 1.9 (s, 3H × 0.80, $-\mathrm{Ar}\mathit{CH_3}$), δ 3.9 (dq, 4H × 0.16, $^{3}J_{\mathrm{H-H}} = 6.9$, $^{3}J_{\mathrm{H-P}} = 25.4$, $-\mathrm{O}\mathit{CH_2}\mathrm{CH_3}$), and δ 6.3−7.4 (multiple, 4H, $-\mathrm{O}\mathit{Ar}\mathrm{CH_3}$ and $-\mathrm{O}\mathit{Ar}\mathrm{P}-$). ^{13}C NMR: δ 16.9 (d, $^{3}J_{\mathrm{C-P}} = 6.0$, $-\mathrm{OCH_2}\mathit{CH_3}$), δ 20.9 (s, $-\mathrm{Ar}\mathit{CH_3}$), δ 62.2 (bs, $-\mathrm{O}\mathit{CH_2}\mathrm{CH_3}$), δ 122.0 (s, $-\mathrm{O}\mathit{Ar}\mathrm{CH_3}$), δ 125.2 (d, $^{1}J_{\mathrm{C-P}} = 190$, $-\mathrm{O}\mathit{ArP}-$), δ 130.4 (s, $-\mathrm{O}\mathit{Ar}\mathrm{CH_3}$), δ 132.4 (s, $-\mathrm{O}\mathit{Ar}\mathrm{P}-$), δ 132.6 (s, $-\mathrm{O}\mathit{Ar}\mathrm{P}-$), δ 133.8 (s, $-\mathrm{O}\mathit{ArCH_3}$), δ 150.4 (s, $-\mathit{OAr}\mathrm{CH_3}$), δ 155.5 (s, $-\mathit{OAr}\mathrm{P}-$). ^{31}P NMR: δ −18.9 (br, 1P × 0.34, $-\mathit{P}(\mathrm{OArP}-)$-$(\mathrm{OArCH_3}){=}\mathit{N}-$), −18.1 (br, 1P × 0.66, $-\mathit{P}(\mathrm{OArCH_3})_2{=}\mathit{N}-$), 18.7 (br, 1P × 0.34, $-\mathrm{Ar}\mathit{P}-$). Elemental analysis: found (calculated for 83% (16.5%/20%) phosphonation of bromines): C, 58.73 (58.93); H, 5.36 (5.35); P, 13.56 (13.55); N, 4.40 (4.61); Br, 0.70 (1.84); Cl, 0.12 (0.00). $M_{\mathrm{n}} = 270\,000$; PDI = 1.5.

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