Organometallics **1991**, *10*, 3819–3825

Synthesis and Reactivity of Cyclotriphosphazenes Bearing Reactive Silane Functionalities: Novel Derivatives via Hydrosilylation Reactions[1]

Harry R. Allcock,* Constance J. Nelson, and William D. Coggio

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received May 7, 1991

Cyclotriphosphazenes with the general structure $N_3P_3(OPh)_5NH(CH_2)_3SiMe_2OEt$ react with lithium aluminum hydride in diethyl ether to produce $N_3P_3(OPh)_5NH(CH_2)_3SiMe_2H$. Subsequent reaction of this species with alkenes in the presence of a platinum catalyst produced new cyclotriphosphazenes bearing alkoxy, siloxy, glycidyl, and ferrocenyl side groups. The yields depended on the type of catalyst and olefin used. Tetramethyl-1,3-divinyldisiloxane–platinum complex (DVDS:Pt) was a more efficient hydrosilylation catalyst than hydrogen hexachloroplatinic acid (CPA). Use of the latter catalyst yielded the silanol $N_3P_3(OPh)_5NH(CH_2)_3SiMe_2OH$, as a side product. This derivative subsequently condensed to produce a ring-linked phosphazene species. The hydrosilylation products were studied by ^{31}P, ^{1}H, and ^{13}C NMR and infrared spectroscopy, elemental analysis, and mass spectrometry. Analogous reactions were investigated with the high-polymeric counterparts. Polymers with the general structure $[NPR_{1.8}(NH(CH_2)_3SiMe_2OEt)_{0.2}]_n$, where R is $-OCH_2CF_3$ or $-OC_6H_5$, were synthesized and allowed to react with $LiAlH_4$. The reduction process induced significant molecular weight decline from phosphorus–nitrogen bond cleavage, which was probably initiated by coordination of the aluminum to the nitrogen atoms in the polymer backbone and the amino side group. The influence of complexing agents, such as 4-(dimethylamino)pyridine (DMAP) and Et_3N, on the reduction reactions was investigated.

We have published a series of papers on the synthesis of cyclic and high-polymeric phosphazenes that bear organosilicon side groups.[2-11] The polymeric species have properties that include low-temperature elasticity, hydrophobicity, and unusual gas permeation behavior. Here we consider the possibility that functionalized organosilicon side groups linked to a polyphosphazene can serve as precursors to other types of organosilyl-containing polyphosphazenes.

Reactive organosilicon groups such as Si–Cl, Si–OH, and Si–OR are widely used in synthetic research. However, the same reactivity which makes these species useful in organosilicon chemistry has prevented their incorporation into polyphosphazenes. Attempts to synthesize cyclic and high-polymeric phosphazenes with such side groups have invariably resulted in the formation of cross-linked materials.[8,12]

In recent years, the Si–H bond has become one of the most useful and versatile functionalities in organosilicon chemistry.[13-15] The driving force for these developments was the discovery that the Si–H bond adds easily across double and triple carbon–carbon bonds in the presence of metal-containing catalysts. Furthermore, unlike Si–Cl, Si–OH, and Si–OR, the Si–H bond is relatively stable to moisture. Thus, it appeared possible that the Si–H functional group might be incorporated into a phosphazene molecule and be used in subsequent reactions to produce new species via hydrosilylation with alkenes. Recently, van de Grampel and co-workers reported the preparation of phosphazene-substituted polysiloxanes via hydrosilylation of allyl-derivatized cyclophosphazenes with polymethylhydrosiloxanes.[16]

Results and Discussion

Small-Molecule Reactions: Preparation of Silane-Derivatized Phosphazene Trimers. Scheme I summarizes the small-molecule studies. Hexachlorocyclotriphosphazene (**1**) was first treated with sodium phenoxide to replace all but one of the chlorine atoms and yield **2**. Pentaphenoxy((3-(dimethylethoxysilyl)propyl)amino)cyclotriphosphazene (**3**) was then prepared via the replacement of the remaining halogen atom in **2** by reaction with $H_2N(CH_2)_3SiMe_2OEt$. The reaction was monitored by ^{31}P NMR spectroscopy and was considered to be complete when the characteristic AB_2 pattern of **2** (δ_A = 22.0 ppm, δ_B = 6.8 ppm, J_{PNP} = 83.3 Hz) changed to the new AB_2 pattern indicative of **3** (δ_A = 17.9 ppm, δ_B = 8.2 ppm, J_{PNP} = 75.5 Hz). The structure of this compound was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR and infrared spectroscopy, elemental analysis, and mass spectrometry.

The reduction of ethoxysilanes, $R_3Si–OEt$, by $LiAlH_4$ to produce organosilanes, $R_3Si–H$, has been reported previously.[17,18] Similarly, reduction of **3** by $LiAlH_4$ in Et_2O at 25 °C, gave the (organosilyl)phosphazene $N_3P_3(OPh)_5(NH(CH_2)_3SiMe_2H)$ (**4**) in good yield. Infrared spectroscopy and thin-layer chromatography were used in tandem to monitor the progress of the reaction. The appearance of the characteristic Si–H infrared absorption at

---

[1] This paper is the 11th from our laboratory on organosilicon derivatives of phosphazenes. For previous papers in this series, see refs 2–11.

[2] Allcock, H. R.; Brennan, D. J.; Allen, R. W. *Macromolecules* **1985**, *18*, 139.

[3] Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M.; Parvez, M. *Organometallics* **1986**, *5*, 2434.

[4] Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, *21*, 1.

[5] Allcock, H. R.; Brennan, D. J.; Dunn, B. S.; Parvez, M. *Inorg. Chem.* **1988**, *27*, 3226.

[6] Allcock, H. R.; Brennan, D. J. *J. Organomet. Chem.* **1988**, *341*, 231.

[7] Allcock, H. R.; Brennan, D. J.; Dunn, B. S. *Macromolecules* **1989**, *22*, 1534.

[8] Allcock, H. R.; Coggio, W. D.; Archibald, R. S.; Brennan, D. J. *Macromolecules* **1989**, *22*, 3571.

[9] Allcock, H. R.; Coggio, W. D. *Macromolecules* **1990**, *23*, 1626.

[10] Allcock, H. R.; Coggio, W. D.; Parvez, M.; Turner, M. L. *Organometallics* **1991**, *10*, 677.

[11] Allcock, H. R.; Coggio, W. D. *Macromolecules*, submitted for publication.

[12] Wissan-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2089.

[13] Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

[14] Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

[15] Chujo, Y.; Ihara, E.; Ihara, H.; Saegusa, T. *Polym. Bul.* **1988**, *19*, 435.

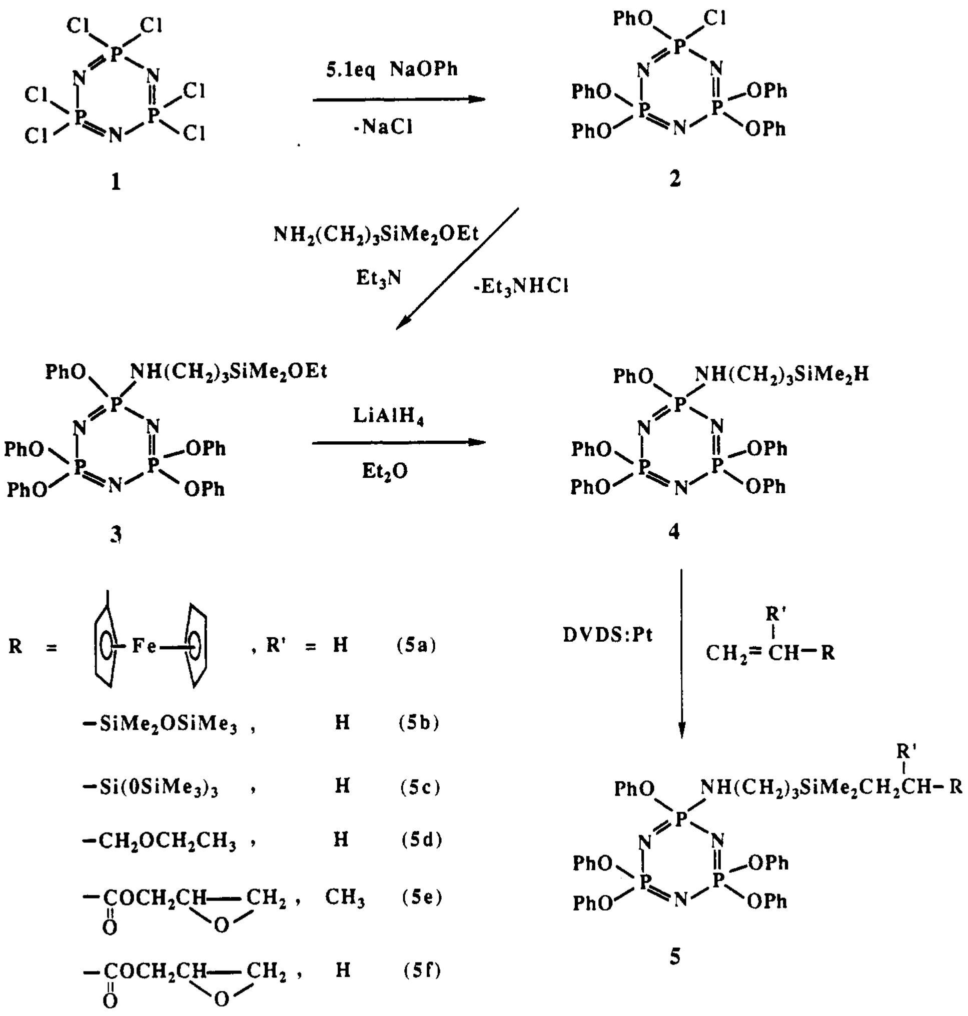
[16] van de Grampel, J. C.; Puyenbroek, R.; Jekel, A. P. *J. Inorg. Organomet. Polym.* **1991**, *1*, 105.

[17] Wu, H.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564.

[18] Voronkov, M. G. In *The Siloxane Bond*; Consultants Bureau: New York, 1978; Chapter 3.

0276-7333/91/2310-3819$02.50/0

Scheme I



(DVDS:Pt = tetramethyl-1,3-divinyldisiloxane platinum-complex)

2114 cm^{-1} and the disappearance of starting material, **3**, as monitored by thin-layer chromatography, confirmed the complete reduction of the ethoxy group. The reaction was usually complete after 6–8 h at 25 °C. No evidence for coordination of aluminum to the phosphazene skeletal nitrogen atoms or of decomposition of the phosphazene ring was detected by ^{31}P NMR spectroscopy. Compound **4**, which is stable to air and atmospheric moisture, was purified by column chromatography and was subsequently recrystallized from pentane at 0 °C. Further reaction details are given in the Experimental Section.

Small-Molecule Reactions: Hydrosilylation with the Silane-Derivatized Phosphazene Trimers. The versatility of the hydrosilylation reaction has been reviewed by Speier, Lewis, and others and is the subject of numerous articles and patents.[14] However, despite the utility of this reaction, no simple, well-understood mechanism for the hydrosilylation process yet exists. One reason for this anomaly lies in the diversity of the catalysts available and in the resultant homogeneous or heterogeneous nature of the reactions.

In this study chloroplatinic acid was used initially as the hydrosilylation catalyst. However, it was found that when **4** was allowed to react with an olefin in the presence of this catalyst in THF at 66 °C, the target product was obtained in only poor yields (i.e. <30%). Analysis of the byproducts formed in these reactions indicated that ring-linked dimers such as **6** had formed via silanol condensation (see Scheme II). The formation of silanol end groups during hydrosilylation reactions that utilize chloroplatinic acid has been reported previously by Boileau and co-workers.[19] In addition, it was found that, with chloroplatinic acid as a catalyst, lengthy induction periods were sometimes required to achieve formation of the product. Moreover, van de Grampel and co-workers reported recently that reproducible results were not obtained when this catalyst was utilized for a similar system.[16]

Thus, in order to circumvent these limitations, other hydrosilylation catalysts were investigated. Tetramethyl-1,3-divinyldisiloxane–platinum complex (DVDS:Pt) was found to be a more efficient hydrosilylation catalyst than chloroplatinic acid. Hydrosilylation reactions catalyzed by DVDS:Pt proceeded under milder conditions and without the formation of dimeric side products such as **6**. As a result, this catalyst was used for the remainder of the study.

As outlined in Scheme I, the reaction between **4** and olefins in the presence of DVDS:Pt gave the corresponding hydrosilylation products **5a–f**. A possible explanation for the increased efficiency of the DVDS:Pt complex compared with chloroplatinic acid is that the platinum in DVDS:Pt exists in the zero oxidation state. This appears to eliminate the need for a reductive induction period and thus increases the reaction rate. The hydrosilylation reactions were carried out in THF at 25–66 °C for times ranging

---

[19] Lestel, L.; Boileau, S. *Polym. Prepr.* **1989**, *30* (1), 133.

Scheme II

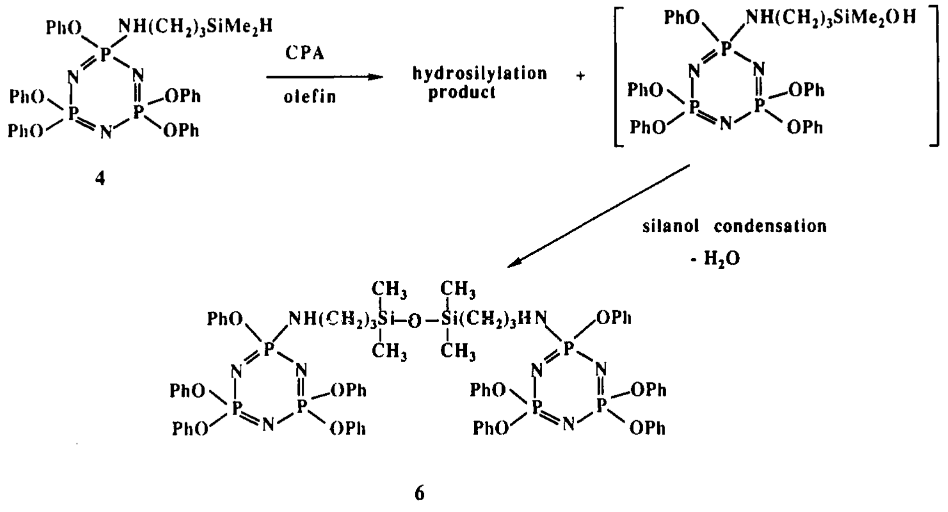


Table I. Analytical Data for 3, 4, and 5a–f

	mass spec, *m/z*		anal., %			
compd	calcd	found	atom	calcd	found	infrared data,[e] cm^{-1}
3	760[a]	714[d]	C	58.41	58.62	1260, 1080, 800
			H	5.71	5.76	
			N	7.37	7.27	
4	716[b]	716	C	58.65	59.04	2114, 1264, 800
			H	5.48	5.47	
			N	7.82	7.48	
5a	928[a]	928	C	60.77	61.34	1260, 798
			H	5.53	5.24	
			N	6.03	5.97	
5b	891[a]	891	C	56.61	53.99[f]	1260, 1050, 800
			H	6.45	6.71	
			N	6.29	5.21	
5c	1038[a]	1038	C	53.14	52.94	1260, 1055, 1026, 1008, 805
			H	6.70	6.57	
			N	5.39	5.91	
5d	802[c]	803	C	59.83	53.40[g]	1264, 804
			H	6.16	6.93	
			N	6.98	6.74	
5e	858[a]	858	C	58.73	58.78	1718, 1260, 799
			H	5.75	5.25	
			N	6.52	6.20	
5f	844[a]	844	C	58.29	57.89	1726, 1260, 797
			H	5.61	5.56	
			N	6.63	6.67	

[a] Electron impact used. [b] Chemical ionization used. [c] +FAB method employed. [d] *m/z* corresponds to loss of ethoxy group from **3**. [e] IR samples taken as thin films on NaCl plates. In addition to the bands reported, all compounds had spectra consistent with the presence of alkyl, aryl, secondary amine, and P=N groups at approximately 2960, 3030, 3450, and 1200 cm^{-1}, respectively. [f] Olefin contained residual divinyl not separable by distillation; this accounts for analytical discrepancy. [g] Product confirmed by NMR, IR, and FAB; however, analysis for carbon was not reproducible.

from 4 h to 2 days. FTIR spectroscopy was utilized to follow the progress of the reaction by monitoring the loss of the Si–H absorption at 2108 cm^{-1} in **4**. The resultant hydrosilylated trimers **5a–f** were isolated in moderate yields by column chromatography, followed by preparative layer chromatography. The products were characterized by FTIR spectroscopy, mass spectrometry, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and elemental analysis. These data are listed in Table I and in the Experimental Section. With the synthesis of **5a–f** accomplished, it seemed possible that similar hydrosilylation reactions would occur readily with analogous high molecular weight polyphosphazenes.

High-Polymer Reactions: Attempted Reduction of the Ethoxysilane Side Group by LiAlH$_4$. As with the cyclic trimer reactions, an incorporation of the Si–H functional group was attempted at the high-polymer level initially via the reduction of the ethoxysilane side group by LiAlH$_4$. Although poly[bis((3-(dimethylethoxysilyl)propyl)amino)phosphazene], $[NP(NH(CH_2)_3SiMe_2OEt)_2]_n$, is accessible, a fully functionalized polymer of this type would have presented too great a complexity for a thorough study. Therefore, in order to simplify the system, cosubstituent polyphosphazenes, with the general structure of $[NP(OR)_{1.8}(NH(CH_2)_3SiMe_2OEt)_{0.2}]_n$, OR = phenoxy (OPh) or trifluoroethoxy (OCH_2CF_3), were synthesized as precursors to the silane-functionalized polymers.

The synthesis of polymers $[NP(OPh)_{1.8}(NH(CH_2)_3SiMe_2OEt)_{0.2}]_n$ (**7**) and $[NP(OCH_2CF_3)_{1.8}(NH(CH_2)_3SiMe_2OEt)_{0.2}]_n$ (**8**) is described in the Experimental Section. The polymers are amorphous, elastomeric materials that are slightly air and moisture sensitive because of the presence of the ethoxysilane group. Thus, it was necessary to protect these materials from the atmosphere in order to prevent cross-linking via hydrolysis and subsequent silanol condensation. For this reason, the attempted reduction of these polymers was carried out in situ (see Experimental Section). However, this approach

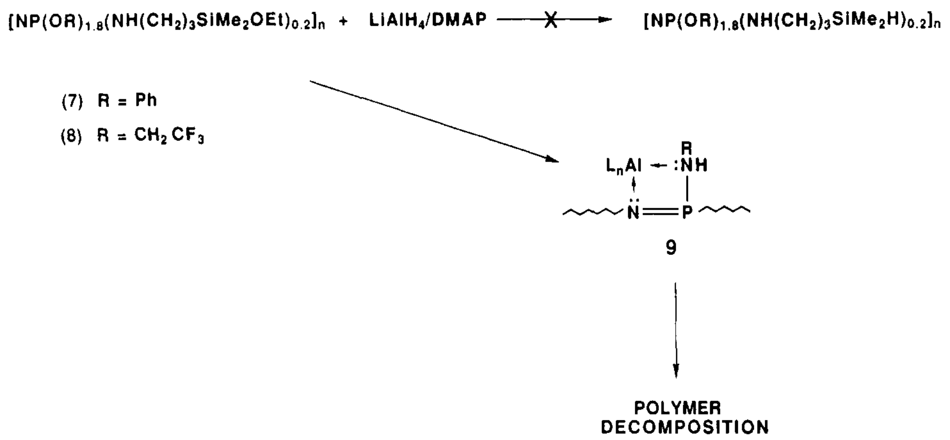
Scheme III

$$\text{(a)}\quad [\mathrm{NP(OR)_2}]_n \xrightarrow[\text{1h}]{\text{4 eq DMAP}} \text{no reaction} \xrightarrow[\text{1d}]{\text{1 eq LiAlH}_4} \text{no reaction}$$

$$\text{(b)}\quad [\mathrm{NP(OR)_2}]_n \xrightarrow[\text{1h}]{\text{1 eq LiAlH}_4} \text{no reaction} \xrightarrow[\text{1d}]{\text{4 eq DMAP}} \text{no reaction}$$

R = Ph or CH_2CF_3

Scheme IV



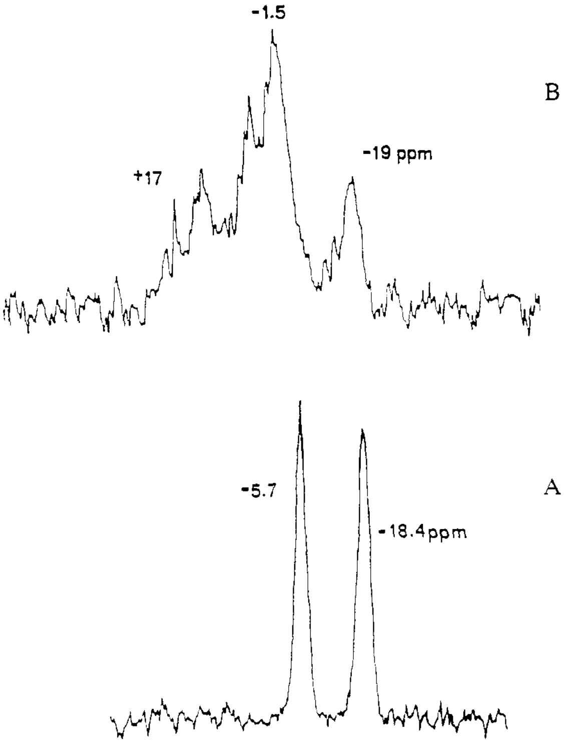


Figure 1. (A) 36.23-MHz ^{31}P NMR spectrum of a cosubstituent polymer with the general structure shown in **7**. Signals at −18.4 and −5.7 ppm are for phosphorus units such as $P(OPh)_2$ and P(NHR)(OPh), respectively. (B) ^{31}P NMR spectrum of polymer **7** after treatment with DMAP/$LiAlH_4$ for 30 min. The broad signals are characteristic of metal coordination to the phosphazene backbone (see ref 20).

proved to be unsuccessful because of the facile coordination of the aluminum, probably to both a backbone nitrogen and a side group nitrogen atom in a bindentate manner (see Scheme IV). Previous studies that involved aminophosphazene polymers report similar coordination reactions.[20,21]

High-Polymer Reactions: Reduction Reactions in the Presence of DMAP. Allcock, Desorcie, and Rutt have reported that bases such as Et_3N are effective for the removal of aluminum that has coordinated to a phosphazene backbone.[20] Thus, the possibility was investigated that a stronger complexing agent, such as 4-(dimethylamino)pyridine (DMAP), might prevent the coordination of aluminum to the polymer backbone.

First, the stability of the polymer backbone to DMAP was studied by the use of control reactions that utilized the single-substituent phosphazene polymers poly[bis(phenoxy)phosphazene], $[NP(OPh)_2]_n$, and poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$, as outlined in Scheme III. The results obtained from these control experiments suggested that these polymers are stable to DMAP/$LiAlH_4$ mixtures under the conditions needed to bring about reduction of the ethoxysilane side group.

Second, similar reactions were conducted by using polymers **7** and **8** (see Scheme IV). The addition of DMAP to each polymer solution resulted in no detectable reaction, as determined by ^{31}P NMR spectroscopy. However, the subsequent addition of $LiAlH_4$ to the phenoxy cosubstituent polymer, **7**, again resulted in the formation of an aluminum–nitrogen complex similar to **9**. This coordination reaction was detected by ^{31}P NMR spectroscopy (see Figure 1).

Addition of $LiAlH_4$ to a solution of the trifluoroethoxy cosubstituent polymer, **8**, and DMAP in THF brought about no detectable reaction, as determined by ^{31}P NMR spectroscopy. No Si–H infrared absorption was detected even after allowing **8** to react with $LiAlH_4$ for 24 h. Moreover, extended exposure of **8** (i.e. 48 h, 25 °C) to the

---

(20) Allcock, H. R.; Desorcie, J. L.; Rutt, J. S. *Organometallics* **1988**, *7*, 612.

(21) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119.

DMAP/$LiAlH_4$ mixture resulted in a gradual decrease in molecular weight. Thus, a slow cleavage of the phosphazene backbone can still occur even in the presence of DMAP. The less effective coordination of aluminum to the phosphazene backbone in **8** compared with **7**, when solutions of both contain DMAP, is probably a consequence of the strong electron-withdrawing ability of the trifluoroethoxy side groups, which decreases the basicity of the backbone nitrogen atoms. However, it is not clear why this electron withdrawal also hinders reduction of the ethoxysilane side group.

Additional studies were carried out with variations in reducing and complexing agents, solvents, and reaction conditions, again with no formation of the Si–H functionality (see Experimental Section).

Attempted Preparation of $RHN(CH_2)_3Si(R')_2H$. Because of the difficulties encountered with the reduction of the ethoxysilane side group at the high-polymer level, attempts were also made to synthesize the free aminosilane group, $RHN(CH_2)_3SiMe_2H$, both as a model reaction and as a possible synthetic intermediate (see Experimental Section). However, this product tends to cyclize and/or polymerize readily during distillation. Serebrennikova and co-workers have reported similar difficulties in attempts to isolate (3-aminopropyl)diethylsilane.[22] Related reports by Massol and co-workers described the room-temperature cyclization of (3-hydroxypropyl)dimethylsilane to cyclo(oxasilapentane) with evolution of hydrogen.[23]

Conclusions

The cyclotriphosphazene $N_3P_3(OPh)_5NH(CH_2)_3SiMe_2H$ was synthesized and subsequently allowed to react with selected olefins, via hydrosilylation in the presence of a platinum catalyst. This same methodology was investigated at the high-polymer level, but it was found that coordination, between the aluminum of the $LiAlH_4$ and the nitrogen atoms in the polymer backbone and the amino side groups, led to chain cleavage.

The stability of $[NP(OPh)_2]_n$ and $[NP(OCH_2CF_3)_2]_n$ to DMAP/$LiAlH_4$ mixtures suggests that a structural prerequisite for coordination of the aluminum to the phosphazene backbone is the presence of an electron-donating side unit, such as an amino group. This supports the hypothesis that aluminum coordinates to the polymer backbone in a bidentate manner, as shown for **9**.

The preparation of Si–H functional polyphosphazenes is also possible via methods that avoid the use of reducing agents. For example, Nakahama and co-workers have reported the synthesis of poly(4-(dimethylsilyl)styrene) but no effort to exploit the silane functional group via hydrosilylation reactions was reported.[24] We have synthesized similar polymers with the general structure $[NP(OC_6H_4SiMe_2H)_x(OPh)_{2-x}]_n$ and $[NP(OC_6H_4SiMe_2H)_x(OC_6H_5Br)_{2-x}]_n$. Although hydrosilylation of these materials was successful, purification of the resultant products proved difficult. In addition, the precursor polymers were found to cross-link slowly even when stored under an inert atmosphere. Thus, although derivatization via hydrosilylation reactions is relatively straightforward for small-molecule cyclotriphosphazenes, further investigations will be required to provide a viable methodology at the high-polymer level.

Experimental Section

Equipment. ^{31}P (36.23 MHz) NMR spectra were obtained with the use of a JEOL FX90Q spectrometer. ^1H NMR (360.0 MHz), ^{13}C NMR (90.0 MHz), and ^{31}P NMR (145.8 MHz) spectra were obtained with a Bruker WM-360 spectrometer. Infrared spectra were recorded by use of a Perkin-Elmer 1710 FTIR spectrophotometer interfaced with a Perkin-Elmer 3600 data station. Gravity-driven chromatography was carried out with the use of 60/200-mesh silica gel under atmospheric conditions.

Materials and Procedures. All reaction mixtures were protected from the atmosphere by dry nitrogen or dry argon (Matheson), with use of standard Schlenk-line techniques. Tetrahydrofuran (THF) (Omnisolv) and diethyl ether (Et_2O) were dried and distilled from sodium benzophenone ketal. *N*-(Trimethylsilyl)allylamine (TMS—$NHCH_2CH{=}CH_2$), dimethylethoxysilane ($HSiMe_2OEt$), vinyltris(trimethylsiloxyl)silane ($CH_2{=}CHSi(OSiMe_3)_3$), vinyldimethylchlorosilane ($CH_2{=}CHSiMe_2Cl$), tetramethyl-1,3-divinyldisiloxane–platinum complex (DVDS:Pt), and potassium trimethylsilanolate ($K^+(OSiMe_3)^-$) were obtained from Petrarch and, where necessary, purified by distillation. Vinylferrocene, glycidyl methacrylate, allyl ethyl ether, and glycidyl acrylate were obtained from Aldrich and were used as received. Hexachlorocyclotriphosphazene was obtained from Ethyl Corp. and was purified by sublimation at 50 °C and 0.1 mmHg. Pentaphenoxymonochlorocyclotriphosphazene (**2**), poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$, and poly(diphenoxyphosphazene), $[NP(OC_6H_5)_2]_n$, were prepared by procedures reported previously.[8,25,26] Phenol (Fisher) was dried via azeotropic removal of water with benzene. Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN.

Synthesis of (3-Aminopropyl)dimethylethoxysilane, $H_2N(CH_2)_3SiMe_2OEt$. This species was prepared via the hydrosilylation reaction between *N*-(trimethylsilyl)allylamine ($Me_3SiNHCH_2CH{=}CH_2$) and dimethylethoxysilane ($Me_2SiHOEt$). The reaction was carried out in a three-necked round-bottomed flask protected from the atmosphere by argon. Dry THF (50 mL) was added to freshly distilled *N*-(trimethylsilyl)allylamine (25 g, 0.19 mol), dimethylethoxysilane (17.7 g, 0.17 mol), and approximately 2 mol % of DVDS:Pt. The reaction mixture was refluxed for 8 h. After this time the reaction mixture was cooled to room temperature, and excess 95% ethanol (25 mL) was added. The reaction mixture was refluxed for an additional 6 h to remove the *N*-(trimethylsilyl) protecting group. The THF was removed under reduced pressure, and the remaining liquid was distilled at 56–58 °C at 10 mmHg to produce 18.6 g (68%) of the desired product. Analytical data are as follows. ^1H NMR ($CDCl_3$): H_2N, 1.0 ppm (s, exchangeable with D_2O); NCH_2, 2.57 ppm (t); CH_2, 1.38 ppm (m); CH_2Si, 0.5 ppm (m); $SiMe_2$, 0.03 ppm (s); OCH_2, 3.58 ppm, (q); OCH_2CH_3, 1.1 ppm (t). ^{13}C NMR: NCH_2, 45.0 ppm; CH_2, 27.0 ppm; CH_2Si, 13.0 ppm; $SiMe_2$, −2.0 ppm; OCH_2, 58.0 ppm; OCH_2CH_3, 18.1 ppm. Mass spec (CI): calcd, *m/z* 161; found, *m/z* 162.

Synthesis of Pentamethylvinyldisiloxane, $CH_2{=}CHSiMe_2OSiMe_3$. Dry THF (150 mL) was protected from the atmosphere by N_2. Vinyldimethylchlorosilane, $CH_2{=}CHSiMe_2Cl$ (15 g, 0.13 mol), and potassium trimethylsilanolate, $K^+(OSiMe_3)^-$ (24.3 g, 0.19 mol), were added, and the solution was refluxed for 8 h. A copious amount of KCl precipitated in the reaction vessel during this time. The salts were filtered off, and the THF was removed carefully under reduced pressure to avoid loss of the desired volatile product. The remaining liquid distilled at 83–91 °C at 760 mmHg. The product was isolated in 52% yield (11.3 g). Analytical data are as follows. ^1H NMR ($CDCl_3$): vinyl, 6.2–5.7 ppm (m); $SiMe_2$, 0.1 ppm (s); $SiMe_3$, −0.05 ppm (s). ^{13}C NMR: CH_2, 139.6 ppm; CH, 131.5 ppm; $SiMe_2$, 1.9 ppm (s); $SiMe_3$, 0.4 ppm.

Synthesis of Pentaphenoxy((3-(dimethylethoxysilyl)propyl)amino)cyclotriphosphazene (3). Compound **2** (35 g, 55 mmol) was dissolved in THF (250 mL). To this solution was

---

[22] Serebrennikova, E. V.; Balaklo-Yusinovich, N. F.; Karepov, A. A.; Vakhrushev, L. P. In *Chemistry, Biochemical Functions and Applications of Pantothenic Acid*; Moiseenok, A. G., Ed. (Engl ed.); presented at the Grodno Symposium, Minsk, USSR, 1977; p 124.

[23] Massol, M.; Barrau, J.; Satge, J.; Bouyssieres, B. *J. Organomet. Chem.* **1974**, *80*, 47.

[24] Hirao, A.; Hatayama, T.; Nakahama, S. *Macromolecules* **1987**, *20*, 1505.

[25] Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

[26] Allcock, H. R.; Mang, M. N.; Dembek, A. A.; Wynne, K. J. *Macromolecules* **1989**, *22*, 4179.

added $\mathrm{Et_3N}$ (5.5 equiv, 30.7 mL, 303 mmol). A solution of (3-aminopropyl)dimethylethoxysilane (9.8 g, 60.7 mmol) in THF (100 mL) was added to the warming solution of **2**. After the mixture had refluxed for 12 h, the product was isolated by filtration through THF-rinsed Fuller's Earth, concentrated, vacuum dried, and recrystallized from pentane to yield pure **3** as a white powder in 75% yield. Exposure to the atmosphere was minimized to avoid the hydrolysis of the labile Si–OEt group. Analytical data are as follows. ^{31}P NMR ($\mathrm{CDCl_3}$): δ_A 17.9 ppm (t, $P\mathrm{OPh(NHR)}$), δ_B 8.2 ppm (d, $P\mathrm{(OPh)_2}$); $^2J_\mathrm{PP}$ = 74.2 Hz. ^{1}H NMR ($\mathrm{CDCl_3}$): phenoxy, 7.12 ppm (m); $H\mathrm{N}$, 2.4 ppm (s, exchangeable with $\mathrm{D_2O}$); $\mathrm{NC}H_2$, 2.57 ppm (t); $\mathrm{C}H_2$, 1.38 ppm (m); $\mathrm{C}H_2\mathrm{Si}$, 0.4 ppm (m); $\mathrm{Si}Me_2$, 0.03 ppm (s); $\mathrm{OC}H_2$, 3.58 ppm (q); $\mathrm{OCH_2C}H_3$, 1.1 ppm (t). ^{13}C NMR: phenoxy, 151, 129, 125, and 121 ppm; $\mathrm{N}C\mathrm{H_2}$, 45.0 ppm; $C\mathrm{H_2}$, 27.0 ppm; $C\mathrm{H_2Si}$, 13.0 ppm; $\mathrm{Si}Me_2$, −2.0 ppm; $\mathrm{O}C\mathrm{H_2}$, 58.0 ppm; $\mathrm{OCH_2}C\mathrm{H_3}$, 18.1 ppm. Other data are listed in Table I.

Synthesis of Pentaphenoxy((3-(dimethylsilyl)propyl)amino)cyclotriphosphazene (4). Compound **3** (15.8 g, 21 mmol) was dissolved in dry $\mathrm{Et_2O}$ (250 mL) and added slowly to a suspension of $\mathrm{LiAlH_4}$ (0.79 g, 21 mmol) in dry $\mathrm{Et_2O}$ (100 mL), which was cooled to 0 °C in an ice bath. The progress of the reaction was monitored by FTIR spectroscopy. The reaction was complete after 6.5 h. The reaction was terminated by *slowly* pouring the mixture into a vigorously stirred 1:1 mixture of $\mathrm{Et_2O}$/10% HCl(aq) cooled to 0 °C. The product was isolated by extraction with $\mathrm{Et_2O}$. The organic layers were dried over $\mathrm{MgSO_4}$ and were filtered and concentrated. The crude oil was purified by column chromatography (1:9 $\mathrm{Et_2O}$/hexane), and the product was recrystallized from pentane to yield product **4** as a white powder. Analytical data are as follows. ^{31}P NMR ($\mathrm{CDCl_3}$): δ_A 17.5 ppm (t, $P\mathrm{OPh(NHR)}$), δ_B 8.7 ppm (d, $P\mathrm{(OPh)_2}$); $^2J_\mathrm{PP}$ = 74.9 Hz. ^{1}H NMR ($\mathrm{CDCl_3}$): phenoxy, 7.12 ppm (m); $H\mathrm{N}$, 2.3 ppm (s, exchangeable with $\mathrm{D_2O}$); $\mathrm{NC}H_2$, 2.57 ppm (t); $\mathrm{C}H_2$, 1.38 ppm (m); $\mathrm{C}H_2\mathrm{Si}$, 0.5 ppm (m); $\mathrm{Si}Me_2$, 0.03 ppm (s); $\mathrm{Si}H$, 3.8 ppm (m). ^{13}C NMR: phenoxy, 151, 129, 125, and 121 ppm; $\mathrm{N}C\mathrm{H_2}$, 45.0 ppm; $C H_2$, 27.0 ppm; $C\mathrm{H_2Si}$, 13.0 ppm; $\mathrm{Si}Me_2$, −2.0 ppm. Other data are listed in Table I.

Synthesis of Pentaphenoxy((3-((2-ferrocenylethyl)dimethylsilyl)propyl)amino)cyclotriphosphazene (5a). This procedure is typical of the method used for all the hydrosilylation reactions. Vinylferrocene (0.3 g, 1.4 mmol) was added to a solution containing a catalytic amount of tetramethyl-1,3-divinyldisiloxane–platinum complex (DVDS:Pt) in THF (50 mL). The mixture was stirred for approximately 1 h. A solution of **4** (0.5 g, 0.70 mmol) in dry THF (20 mL) was then added via an addition funnel. An FTIR spectrum of the reaction mixture, after 12 h at reflux, showed complete loss of the Si–H peak at 2108 cm^{-1}. The product was purified by column chromatography (1:9 $\mathrm{Et_2O}$/hexane) followed by preparative layer chromatography (1:4 $\mathrm{Et_2O}$/hexane) to yield the desired product **5a** as a dark oil. Analytical data[27] are as follows. ^{1}H NMR ($\mathrm{CDCl_3}$): $\mathrm{SiC}H_2$, 0.9 ppm (t); $\mathrm{C}H_2\mathrm{Cp}$, 2.3 ppm (m); $\mathrm{CH_2}Cp$, 4.3 (s), 4.1 ppm (m). ^{13}C NMR: $\mathrm{Si}C\mathrm{H_2}$, 14.1 ppm; $C\mathrm{H_2Cp}$, 26.0 ppm; $\mathrm{CH_2}Cp$, 73.3, 71.7, 67.7, and 67.3 ppm. Other data are listed in Table I.

Synthesis of Pentaphenoxy((3-((2-(pentamethyldisiloxanyl)ethyl)dimethylsilyl)propyl)amino)cyclotriphosphazene (5b). Undiluted pentamethylvinyldisiloxane (0.34 g, 1.9 mmol) was added via syringe to a catalytic amount of DVDS:Pt in dry THF (50 mL). Compound **4** (0.7 g, 0.98 mmol) in dry THF (20 mL) was added to this solution, and the mixture was refluxed for 4.5 h. An IR spectrum of the reaction mixture showed no Si–H peak. The product was isolated by column chromatography (1:4 $\mathrm{Et_2O}$/hexane) followed by prep TLC (1:1 $\mathrm{Et_2O}$/hexane) to give product **5b** as a light yellow oil. Analytical data[27] are as follows. ^{1}H NMR ($\mathrm{CDCl_3}$): $\mathrm{SiC}H_2\mathrm{C}H_2\mathrm{Si}$, 0.3 ppm (m); $\mathrm{Si}Me_2$, 0.1 ppm (s); $\mathrm{OSi}Me_3$, −0.05 ppm (s). ^{13}C NMR: $\mathrm{Si}C\mathrm{H_2}C\mathrm{H_2Si}$, 6.7 ppm, 9.3 ppm; $\mathrm{Si}Me_2$, 1.8 ppm (s); $\mathrm{OSi}Me_3$, −0.5 ppm (s). Other data are listed in Table I.

Synthesis of Pentaphenoxy((3-((2-(tris(trimethylsiloxy)silyl)ethyl)dimethylsilyl)propyl)amino)cyclotriphosphazene (5c). Undiluted vinyltris(trimethylsiloxy)silane (1.3 g, 4.0 mmol) was added to a catalytic amount of DVDS:Pt in dry THF (50 mL). After a 0.5-h induction period, **4** (1.0 g, 1.4 mmol) dissolved in dry THF (30 mL) was added dropwise, and the solution was heated for 12 h. No Si–H peak was detected by IR spectroscopy after this time. Following separation by extraction, the crude product was purified by column chromatography (1:4 $\mathrm{Et_2O}$/hexane). Product **5c** was isolated as a noncrystallizable oil in 52% yield. Analytical data[27] are as follows. ^{1}H NMR ($\mathrm{CDCl_3}$): $\mathrm{SiC}H_2\mathrm{C}H_2\mathrm{Si}$, 0.3 ppm (m); $\mathrm{Si(OSi}Me_3)_3$, 0.1 ppm (s). ^{13}C NMR: $\mathrm{Si}C\mathrm{H_2}C\mathrm{H_2Si}$, 6.7, 9.3 ppm; $\mathrm{Si(OSi}Me_3)_3$, 1.8 ppm (s). Other data are listed in Table I.

Synthesis of Pentaphenoxy((3-((2-(2-oxabutyl)ethyl)dimethylsilyl)propyl)amino)cyclotriphosphazene (5d). Undiluted allyl ethyl ether (0.3 mL) was added to a catalytic amount of DVDS:Pt in 50 mL of dry THF. After a 15-min induction period, the trimer **4** (0.7 g, 0.98 mmol) in 20 mL of dry THF was added, and the reaction mixture was heated for 12 h. The reaction was monitored by IR spectroscopy and terminated when no Si–H peak at 2108 cm^{-1} was detected. The compound was isolated and purified by column chromatography and preparative scale LC (1:1 $\mathrm{Et_2O}$/hexane) to give pure **5c** as an oil. Analytical data[27] are as follows. ^{1}H NMR ($\mathrm{CDCl_3}$): $\mathrm{SiC}H_2$, 0.4 ppm (m); $\mathrm{SiCH_2C}H_2$, 1.6 ppm (m); $\mathrm{SiCH_2CH_2C}H_2\mathrm{O}$, 3.4 ppm (t); $\mathrm{OC}H_2$, 3.4 ppm (q); $\mathrm{OCH_2C}H_3$, 1.2 ppm (t). ^{13}C NMR: $\mathrm{Si}C\mathrm{H_2}$, 12.1 ppm; $\mathrm{SiCH_2}C\mathrm{H_2}$, 15.1 ppm; $\mathrm{SiCH_2CH_2}C\mathrm{H_2O}$, 66.1 ppm; $\mathrm{O}C\mathrm{H_2}$, 73.6 ppm; $\mathrm{OCH_2}C\mathrm{H_3}$, 24.2 ppm. Other data are listed in Table I.

Synthesis of Pentaphenoxy((3-((2-methyl-2-((glycidyloxy)carbonyl)ethyl)dimethylsilyl)propyl)amino)cyclotriphosphazene (5e). Glycidyl methacrylate (0.4 mL, 2.8 mmol) was stirred with DVDS:Pt in dry THF (30 mL). A solution of trimer **4** in 20 mL of dry THF (1.0 g, 1.4 mmol) was added via an addition funnel and the solution refluxed for 12 h. IR spectroscopy was used to monitor loss of the Si–H peak. The product, **5e**, was purified by column chromatography (1:4 EtAc/hexane) followed by preparative scale LC (2:3 EtAc/hexane) and isolated as a noncrystallizable oil. Analytical data[27,28] are as follows. ^{1}H NMR ($\mathrm{CDCl_3}$): $\mathrm{SiC}H_2$, 0.65 ppm; 1.2 ppm (m); $\mathrm{C}H\mathrm{CO_2}$, 1.2 ppm (t); $\mathrm{C}H_3$, 1.4 ppm (s); $\mathrm{OC}H_2$, 3.85, 4.4 ppm (m); $\mathrm{C}H\mathrm{CH_2O}$, 3.2 ppm (m); $\mathrm{CHC}H_2\mathrm{O}$, 2.6, 2.8 ppm (m). ^{13}C NMR: $\mathrm{Si}C\mathrm{H_2}$, 20.8 ppm; $C\mathrm{HCO_2}$, 26.0 ppm; $C\mathrm{H_3}$, 31.0 ppm; $\mathrm{O}C\mathrm{H_2}$, 65.0 ppm; $C\mathrm{HCH_2O}$, 50.0 ppm; $\mathrm{CH}C\mathrm{H_2O}$, 45.0 ppm; $C\mathrm{{=}O}$, 178.0 ppm. Other data are listed in Table I.

Synthesis of Pentaphenoxy((3-((2-((glycidyloxy)carbonyl)ethyl)dimethylsilyl)propyl)amino)cyclotriphosphazene (5f). Glycidyl acrylate (0.7 mL, 5.6 mmol) was mixed with DVDS:Pt in 30 mL of dry THF. To this solution was added **4** (2.0 g, 2.8 mmol) in 20 mL of dry THF. An IR spectrum of the reaction mixture showed loss of the Si–H peak after 18 h of reflux. Product **5f** was purified to yield an oil by column chromatography (1:4 EtAc/hexane) and subsequent preparative scale LC (2:3 EtAc/hexane). Analytical data[27,28] are as follows. ^{1}H NMR ($\mathrm{CDCl_3}$): $\mathrm{SiC}H_2$, 0.35, 0.85 ppm (m); $\mathrm{C}H_2\mathrm{CO_2}$, 1.2, 1.3 ppm (m); $\mathrm{OC}H_2$, 4.0, 4.4 ppm (m); $\mathrm{C}H\mathrm{CH_2O}$, 3.2 ppm (m); $\mathrm{CHC}H_2\mathrm{O}$, 2.6, 2.7 ppm (m). ^{13}C NMR: $\mathrm{Si}C\mathrm{H_2}$, 10.0 ppm; $C\mathrm{H_2CO_2}$, 28.0 ppm; $\mathrm{O}C\mathrm{H_2}$, 65.0 ppm; $C\mathrm{HCH_2O}$, 50.0 ppm; $\mathrm{CH}C\mathrm{H_2O}$, 45.0 ppm; $C\mathrm{{=}O}$, 178.0 ppm. Other data are listed in Table I.

Synthesis of Polymer 7. Polymer **7** was prepared by a procedure modified slightly from that reported in ref 8. In a typical reaction designed to replace 90% of the chlorine atoms in $[\mathrm{NPCl_2}]_n$ by an alkoxy or aryloxy substituent, poly(dichlorophosphazene) (3.0 g, 0.052 mol) was dissolved in dry THF (250 mL), and the reaction was protected from the atmosphere by dry argon. Sodium phenoxide (0.047 mol), prepared by the interaction of dry phenol (4.4 g, 0.047 mol) with sodium metal (1.3 g, 0.05 mol) in THF (75 mL), was added dropwise over a 1.5-h period to the polymer solution. The reaction mixture was then warmed to 50 °C for approximately 12 h. After this time the ^{31}P NMR spectrum of the reaction mixture consisted of a single broad resonance at approximately −20 ppm. Dry $\mathrm{Et_3N}$ (10.5 g, 0.10 mol) and undiluted $\mathrm{H_2N(CH_2)_3SiMe_2OEt}$ (1.7 g, 0.01 mol) were then added

---

(27) The NMR data reported for compounds **5a–f** are for new signals associated with the side group after the hydrosilylation had occurred. The chemical shifts associated with the phosphazene ring and phenoxy and aminopropyl side groups did not change significantly from the values reported for **3** or **4**.

(28) Some of the protons in the glycidyl methacrylate (**5e**) and the glycidyl acrylate (**5f**) derivatives are diastereotopic. As a result, several of the signals reported in this section have two chemical shift values to account for the different protons.

to the solution of the partially substituted polymer. The reaction mixture was refluxed for an additional 15 h. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. The reaction was terminated when no further changes in the ^{31}P NMR spectra were detected. The ^{31}P NMR spectrum contained peaks at −4.5 and −18.5 ppm for the *P*(NHR)(OPh) and *P*$(OPh)_2$ units, respectively.

Synthesis of Polymer 8. In a manner similar to that described for the preparation of 7, poly(dichlorophosphazene) (3.0 g, 0.052 mol) was dissolved in dry THF (250 mL) and was protected from the atmosphere by dry argon. To this solution, the addition of sodium trifluoroethoxide (0.047 mol), prepared from the interaction of dry trifluoroethanol (4.7 g, 0.047 mol) and sodium metal (1.3 g, 0.05 mol) in THF (75 mL), was carried out dropwise over a 1.5-h period. The reaction mixture was warmed to 50 °C for approximately 12 h. After this time the ^{31}P NMR spectrum of the reaction mixture consisted of a single broad resonance at approximately −12 ppm. To this solution was added dry Et_3N (10.5 g, 0.10 mol) and undiluted $H_2N(CH_2)_3SiMe_2OEt$ (1.7 g, 0.01 mol). The reaction mixture was refluxed for an additional 15 h. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. The reaction was terminated when no additional changes in the ^{31}P NMR spectrum were detected. The spectrum contained peaks at −0.5 and −7.9 ppm for the *P*(NHR)(OCH_2CF_3) and *P*$(OCH_2CF_3)_2$ units, respectively.

Attempted Reduction of 7 or 8 by $LiAlH_4$. A THF solution of 7 or 8 (1.0 g, 75 mL) was added slowly to a vigorously stirred suspension of $LiAlH_4$(s) in THF cooled to 0 °C with an ice bath. The evolution of H_2 wad detected throughout this addition. After the addition was complete (20 min), the mixture was analyzed by ^{31}P NMR spectroscopy. The NMR spectra of these reaction mixtures consisted of broad signals over a 30–50 ppm sweep width. A typical spectrum is shown in Figure 1. The reaction mixtures were subjected to a *slow* addition of methanol (5 mL) to deactivate any unreacted $LiAlH_4$. The solution was concentrated by partial removal of THF, and the product was precipitated into excess methanol. No polymeric material was isolated. The white solids, isolated by filtration, became insoluble on drying. GPC analysis of the soluble fractions suggested that extensive molecular weight decline had occurred. These materials were believed to be oligomeric products that contained aluminum species coordinated to the phosphazene backbone in a manner similar to the structure depicted for 9.

Attempted Reduction of 7 or 8. Additional reducing and complexing agents, solvents, and reaction conditions for the reduction of polymers 7 and 8 were studied. For example, $BH_3 \cdot THF$ was investigated as a possible alternative to $LiAlH_4$. The smaller boron atom cannot participate in the bidentate coordination necessary to form complex 9. Although complexation was not detected, this species was ineffective for the reduction of the ethoxysilane side groups. The use of other reducing agents such as $NaBH_4$, $[(CH_3)_2CHCH_2]_2AlH$, $LiHBEt_3$, and KH, alone or in combination with complexing agents such as TMEDA or Et_3N under various reaction conditions, proved unsuccessful.

Attempted Preparation of a Free Silane Moiety. In an effort to circumvent the difficulties encountered with the attempted reduction of the ethoxysilane side group at the high-polymer level, attempts were made to synthesize a free silane group. The attempted preparation of a silane moiety via reduction of the R_3 group in a compound of general structure $R_1NH(CH_2)_3Si(R_2)_2R_3$ was investigated. The compounds studied include the following: R_1 = H, R_2 = CH_3, and R_3 = OEt; R_1 = $SiMe_3$, R_2 = CH_3 or OPh, and R_3 = Cl; R_1 = CH_3, R_2 = CH_3, and R_3 = OEt; R_1 = CH_3, R_2 = CH_3 or OPh, and R_3 = Cl. For example, when $NH_2(CH_2)_3SiMe_2OEt$ (0.5 g, 0.003 mol) was treated with $LiAlH_4$ (0.09 g, 0.002 mol) in Et_2O with stirring in a room-temperature water bath for 12 h, the reaction mixture showed the characteristic Si–H infrared absorption at 2109 cm^{-1}. The reaction solution was extracted with a 2-propanol/NaOH/NH_4Cl solution and dried with $MgSO_4$. However, attempted isolation of the purified, free silane group by fractional vacuum distillation was unsuccessful (see refs 22 and 23). Similar attempts to obtain this free silane by use of sterically hindered silyl and/or amino groups with a variety of reducing agents and reaction conditions were also unsuccessful.

Preparation of Poly[*p*-(dimethylsilyl)phenoxy:phenoxy] Cosubstituent Polymers. Preparation of these polymers was carried out by using a synthetic methodology typical of that published in ref 8. The reactions were carried out with use of either a phenoxy:*p*-bromophenoxy cosubstituent polymer or the *p*-bromophenoxy homopolymer. For example, poly[bis(*p*-bromophenoxy)phosphazene] (2.1 g, 5.4 mmol) was dissolved in dry THF (100 mL) and the solution cooled to −78 °C (dry ice/acetone bath). To this solution was added slowly *n*-butyllithium (7.0 mL of a 1.6 M solution, 11.3 mmol, 2.1 equiv) via syringe. After 10 min, a solution of freshly distilled dimethylchlorosilane (3.9 g, 42 mmol) in THF (20 mL) was added dropwise. The reaction solution was then stirred and allowed to warm to room temperature for 12 h. The reaction solution was then concentrated to 75–100 mL and the polymer isolated by precipitation into EtOH. The white, elastomeric polymer was minimally dried and stored under an inert atmosphere. Analytical data are as follows. FTIR: Si–H at 2117 cm^{-1}. ^1H NMR ($CDCl_3$): phenoxy, 6.4–7.1 ppm (m), Si–*H*, 4.2 ppm (m); Si–*Me*, 0.1 ppm (s). Anal. Calcd: C, 49.38; H, 4.99; N, 3.89; Br, 13.32. Found: C, 49.44; H, 4.82; N, 3.68; Br, 12.35.

Hydrosilylation of Poly[(*p*-(dimethylsilyl)phenoxy)(*p*-bromophenoxy)phosphazene]. The silane polymer (0.25 g, 0.7 mmol) was dissolved in THF (150 mL), and a solution of vinyltris(trimethylsiloxy)silane (3.4 equiv, 2.4 mmol) and a catalytic amount of DVDS:Pt in THF (50 mL) was added at room temperature. After 9 h of stirring, FTIR analysis showed quantitative loss of the Si–H stretch. The product was isolated as a dark brown/black elastomeric material; however, purification of the product polymer proved difficult. Repeated precipitations from THF into MeOH and H_2O did not remove the Pt^0 impurity. Exposure of this polymer to Ph_3P solutions in THF was also unsuccessful. Further purification attempts resulted in product decomposition and/or cross-linking.

Acknowledgment. We thank the Air Force Office of Scientific Research for the support of this work.

Registry No. 1, 940-71-6; 2, 5032-39-3; 3, 135928-62-0; 4, 135928-63-1; 5a, 135928-69-7; 5b, 135928-64-2; 5c, 135928-65-3; 5d, 135928-66-4; 5e, 135928-67-5; 5f, 135928-68-6; vinylferrocene, 1271-51-8; pentamethylvinyldisiloxane, 1438-79-5; vinyltris(trimethylsiloxy)silane, 5356-84-3; allyl ethyl ether, 557-31-3; glycidyl methacrylate, 106-91-2; glycidyl acrylate, 106-90-1; sodium phenoxide, 139-02-6.