Organosilicon derivatives
of cyclic and high polymeric phosphazenes *

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Abstract

A new class of compounds is reviewed, the members of which are hybrids of organosilicon and organophosphazene species. They are synthesized either by the reaction of organosilicon halides with organocopper-phosphazene intermediates, or by the interaction of organosilyl or organosiloxy Grignard reagents with chlorophosphazenes. Several of the cyclic trimeric phosphazenes prepared in this way were polymerized by heating to give linear high polymeric phosphazenes with organosilicon side groups.

Introduction

The organometallic chemistry of phosphazenes is an emerging area of research. Recent reports have described lithio-, organocopper-, carboranyl-, metallocenyl-, and transition metal-carbonyl derivatives of cyclic and high polymeric phosphazenes [1]. Most recently [2–6], a number of phosphazenes have been synthesized that bear organosilicon units as side groups, and these promise to be the forerunners of a broad new class of hybrid systems in which the properties of phosphazenes are combined with those of organosilicon compounds. The significance of this development extends beyond the search for new small molecule structures; it provides an opportunity for the synthesis and utilization of unusual high polymers that blend the properties of poly(organophosphazenes) and poly(organosiloxanes).

The chemistry of small molecules is connected to that of macromolecules in two ways. First, macromolecules must be synthesized from small molecules and, in this sense, chemistry carried out at the small-molecule level eventually determines the structure and properties of the high polymers. Second, small-molecule chemistry is

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* This paper is dedicated to Professor Colin Eaborn on the occasion of his 65th birthday, with much appreciation for the part he played in introducing one of us (H.R.A.) to the field of organometallic chemistry.

usually less complex than its counterpart at the macromolecular level with respect to synthesis, mechanisms, and characterization. Hence, the use of small-molecules as models for macromolecules forms an important part of polymer chemistry, particularly for systems such as those described here, where the science is still at the long-range, exploratory stage.

Phosphazene chemistry is the study of compounds that contain alternating phosphorus and nitrogen atoms in the skeleton [7]. Most of the hundreds of compounds in this class have structures that can be summarized by formula **1**,
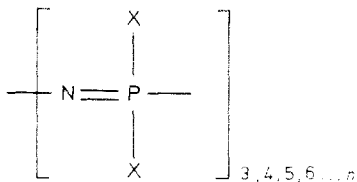

(**1**)

where X is an inorganic unit, such as fluorine, chlorine, cyano, azido, etc., or an organic or organometallic group. The small molecules in the polymeric series (where $n = 3$ to at least 50) are cyclic, although linear, end-capped species are also known. The high polymers (where n may be 15000 or more) are assumed to be linear, although giant macrocyclic structures may also exist.

The high polymers are prepared from small-molecules, such as cyclic trimers, by heating at elevated temperatures (210–300 °C). At even higher temperatures, the macromolecules can depolymerize to small-molecule rings. The similarity to poly(organosiloxane) equilibration reactions is obvious. However, the feature that most distinguishes polyphosphazene chemistry from polysiloxane chemistry is the ease with which side group substitution reactions can be carried out without cleavage of the cyclic oligomeric or high polymeric skeletal bonds. This is a critical factor that has allowed the synthesis of many more different classes of cyclo- and poly-phosphazenes than are accessible in the siloxane system.
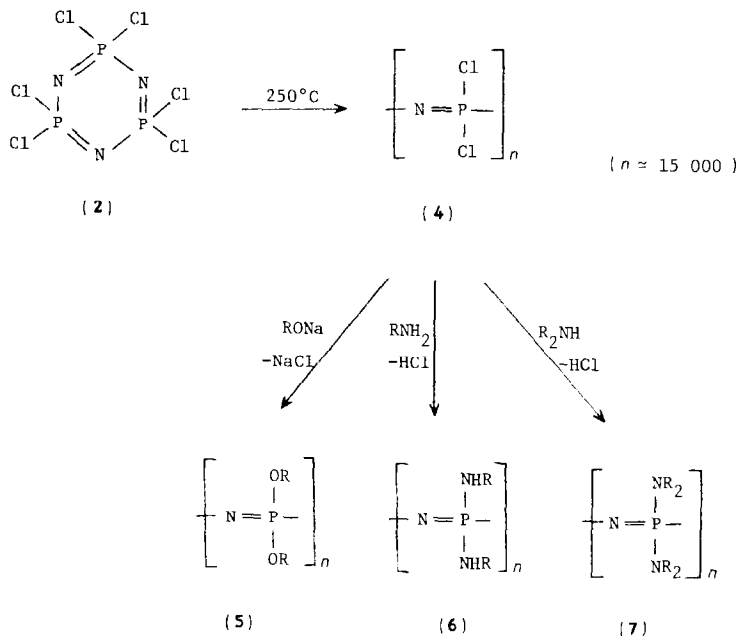
The substitution pathways for cyclic and high polymeric phosphazenes usually start from chloro- or fluoro-phosphazenes (X = Cl or F in structure **1**). Beginning in
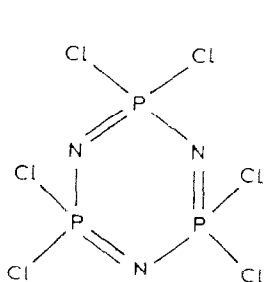
(**2**)
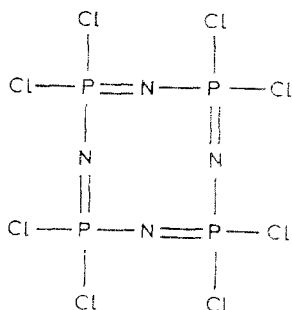
(**3**)

Scheme 1

the mid-1950's, compounds such as **2** or **3** were used as substrates for nucleophilic substitution reactions in which the halogen atoms were replaced by alkoxy, aryloxy, or amino groups to yield stable organophosphazene derivatives. Much activity was evident in the study of substitution mechanisms and patterns of halogen replacement (*gem*, non-*gem*, *cis* or *trans*).

In the mid-1960's, we were able to find reaction conditions that allows the cyclic trimer, **2**, to be polymerized to an uncrosslinked, organic solvent-soluble high polymer (**4**) [8]. This polymer proved to be an excellent reactive macromolecular intermediate for nucleophilic substitution reactions [9]. As shown in Scheme 1, treatment with metal alkoxides or aryloxides, or with primary or secondary amines, allowed replacement of all the chlorine atoms by organic groups. The resultant poly(organophosphazenes) are stable in the atmosphere. The chemical and physical properties vary with the types of organic side groups present, and different species are elastomers, fiber-formers, membrane-formers, hydrophobic or water-soluble, bio-active or bio-inert [10]. Approximately 300 different higher polymeric derivatives are now known, and several are produced on a manufacturing scale for use in advanced engineering applications [11].

Two additional aspects of this chemistry should be noted. First, it is now known that phosphazene cyclic trimers that bear alkyl, aryl, carboranyl, or metallocenyl side groups, in addition to chloro or fluoro units, can be polymerized to the corresponding high polymers. This provides a route for a further diversification of the available macromolecular structures [12,13]. Second, organic chemistry can be carried out on side groups that are attached to the ring or chain in order to modify the chemical and physical characteristics of the system. For example, diacetone glucosyl units attached to a polyphosphazene chain can be deprotected by treatment

with aqueous acid [14]. Nitration and reduction of phenoxyphosphazenes can be accomplished, followed by diazotization [15]. Schiff's base derivatives can be formed [16]. Many of these side group transformations have been used to prepare bioactive or biocompatible polymers for biomedical investigations [10].

It was against the background of these developments that we recently began a program to synthesize cyclic phosphazenes with organosilicon side groups [2–5]. The objective was to prepare organosilylcyclophosphazenes that might serve as structural and reaction models for the corresponding high polymers and would, at the same time, function as "monomers" for polymerization to the corresponding high polymers. It was perceived that, if these polymers could be prepared, they would be interesting hybrid structures with some of the properties of polyphosphazenes combined with features typical of poly(organosiloxanes).

Cyclic trimeric organosilylphosphazenes

The compounds shown as **8–16** have been synthesized by means of organometallic-substitution chemistry [2,4]. Two synthetic approaches have been developed, and these are illustrated in Scheme 2. The first method involves the interaction of
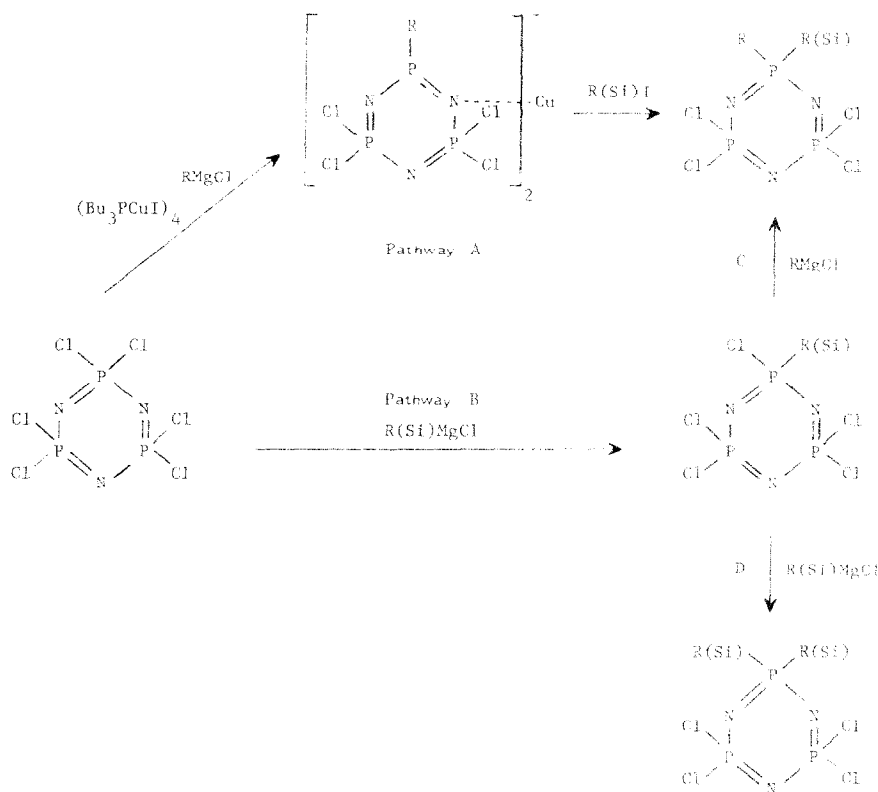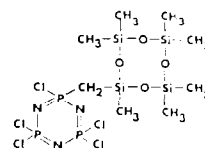

Scheme 2. R(Si) = CH_2SiMe_3, $CH_2SiMe_2OSiMe_2$, $CH_2Si(Me)(OSiMe_2)_3O$; R = CH_3, C_2H_5, i-C_3H_7, n-C_4H_9, t-C_4H_9, neo-C_5H_{11}, C_6H_5.
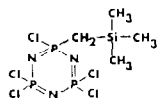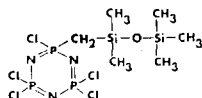
(8) (9) (10)
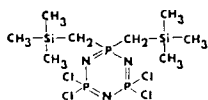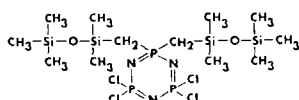
(11) (12) (13)

(14) (15) (16)

organometallic phosphazenes with organosilyl halides (Pathway A). The second requires the reaction of organosilyl or organosiloxy Grignard reagents with chloro-phosphazenes (Pathway B).

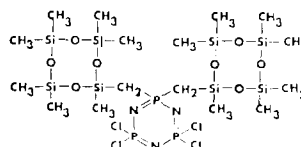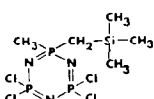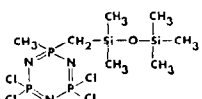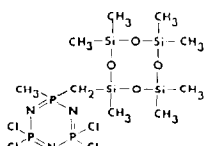These reactions lead to the formation of three different types of derivatives: (a) cyclic trimers that bear one organosilicon side group and five chloro units per ring; (b) those with two geminal organosilicon groups and four chlorine atoms per ring; and (c) species with one organosilicon moiety, a geminal alkyl or aryl group, and four chlorine atoms. This last class includes a series of compounds (of which **14** is the first member), in which the alkyl group can also be ethyl, isopropyl, n-butyl, t-butyl, neopentyl, or phenyl. Species of this type are prepared by the reactions of the appropriate Grignard reagents with compound **8** (Pathway B + C), or (in the case of t-butyl or neopentyl) of an organocopper-phosphazene with trimethylsilyl-methylene iodide (Pathway A). It will be shown that the different structures markedly influence the ability of the cyclophosphazene to undergo ring-opening polymerization.

Halogen-replacement reactions of organosilyl and organosiloxy cyclic phosphazenes

The reactivity of the P–Cl bonds in species, such as **8–16**, is a subject of some importance. Although the chlorine atoms must be present in order to allow ring-opening polymerization to the polyphosphazene, they must eventually be replaced in order to ensure the hydrolytic stability of the final polymer. Thus, species **8–16** are convenient models for the replacement of chlorine by hydrolytic stabilization groups, such as trifluoroethoxy.

Phosphazenes **8–16** (and other alkyl and aryl derivatives analogous to **14**) react with sodium trifluoroethoxide by two different pathways, depending on the reaction
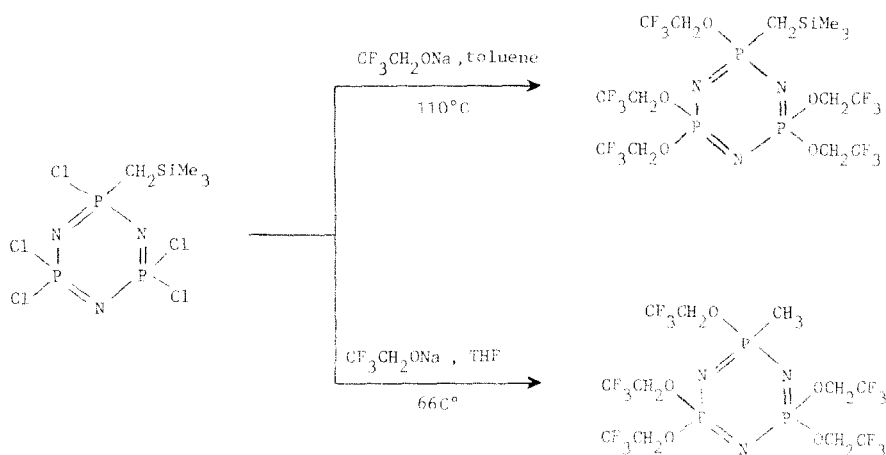
Scheme 3

solvent used [2,4]. One pathway allows halogen replacement without the loss of organosilicon groups. The other involves both replacement of chlorine and cleavage of carbon–silicon bonds (Scheme 3)

Halogen replacement without carbon–silicon bond cleavage can be brought about by the use of a nonpolar solvent, such as toluene, at 110 °C. This process has been used to prepare the trifluoroethoxy derivatives of species **8, 9, 11, 12, 14** (and its analogues), and **15**. However, even in toluene, those compounds that bear cyclotetrasiloxane side groups undergo both PCH_2–Si and Si–O bond cleavage to give phosphazenes that bear a methyl group in place of the methylenesiloxy units. Use of a more polar solvent, such as tetrahydrofuran (at 66 °C), brought about carbon–silicon bond cleavage with all the organosilicon derivatives. The use of dioxane as a solvent at 25 °C provides a pattern intermediate between those found for toluene and for tetrahydrofuran.
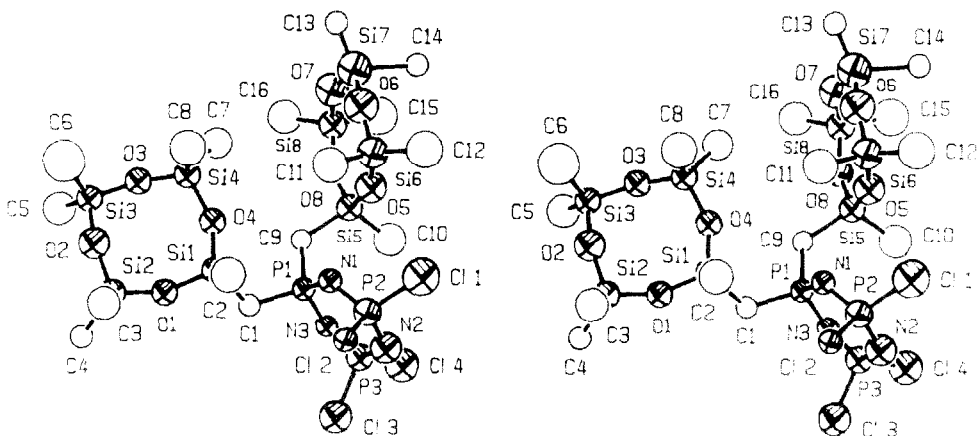
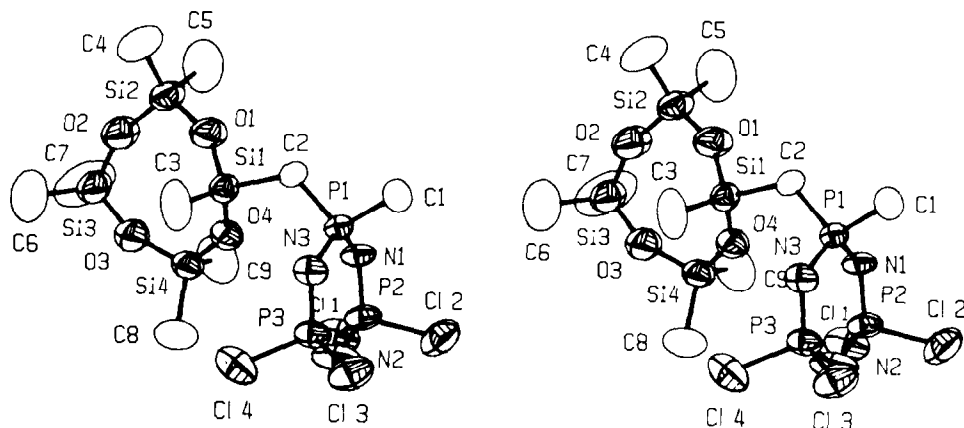Fig. 1. Stereo ORTEP representation of the molecular structure of compound 13.

Fig. 2. Stereo ORTEP drawing of the molecular structure of compound **16**.

Structural studies

The structures of the trimers discussed here have been studied by a combination of ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, infrared spectroscopy, mass spectrometry, and microanalysis. In addition, single crystal X-ray studies have been carried out for compounds **10**, **11**, **13**, and **16**, and for gem-$N_3P_3Cl_4(CH_2SiMe_3)(t-C_4H_9)$. A detailed discussion of the structural parameters has appeared elsewhere [2,4]. The conformations assumed by the siloxane rings in the hybrid cyclophosphazene-cyclosiloxanes, **13** and **16**, are of some interest. These conformations are illustrated in the stereo-ORTEP diagrams shown in Fig. 1 and 2.
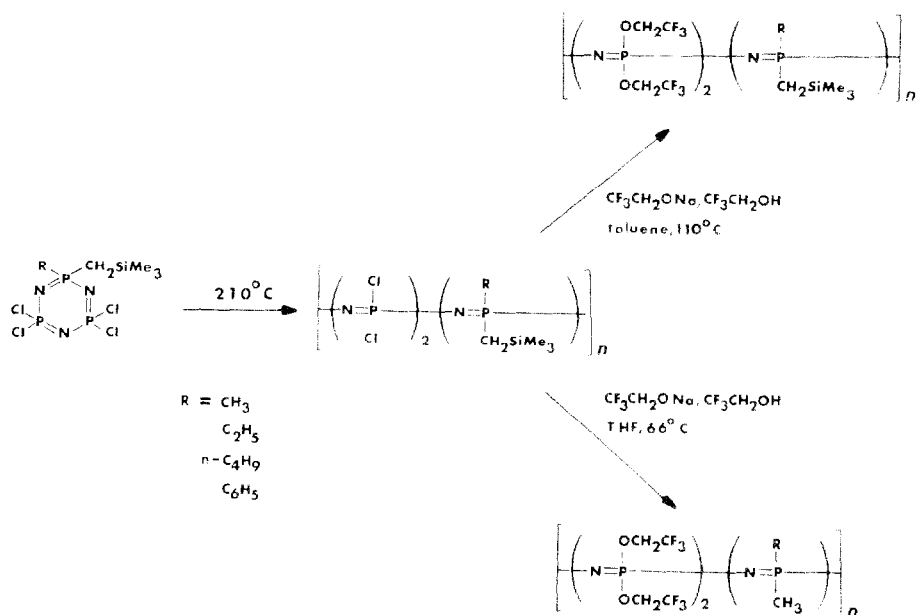
The cyclotetrasiloxane rings in **13** and **16** are puckered. In species **13**, two different puckering modes are evident: a slight boat distortion in one ring and a slight chair distortion in the other. In **16**, the single cyclotetrasiloxane rings adopts a boat conformation. The phosphazene rings in these molecules are distorted somewhat to accommodate the bulk of the cyclotetrasiloxane substituents. The C–P–C exocyclic angles in **13** and **16** are widened to 106.3° and 105.5°, respectively, compared to the 101.5° angle found in $(NPCl_2)_3$ (**2**).

Polymerization and macromolecules

The polymerization of compound **2** to poly(dichlorophosphazene) (**4**) requires rather drastic reaction conditions (210–250°C in the molten state for several hours). It was important to determine if the organosilicon groups attached to compounds **8–16** would survive under these conditions.

Siloxane derivatives, **9**, **10**, **12**, and **13** underwent PCH_2–Si and Si–O bond cleavage in preference to polymerization. Other recent work [17] has demonstrated the sensitivity of Si–O bonds to reactions with phosphazene P–Cl bonds at elevated temperatures.

However, five of the nine compounds, species **8**, **11**, **14**, **15**, and **16**, polymerized when heated at 210–250°C without interference from side reactions [3], as did the counterparts of **14**, in which C_2H_5, n-C_4H_9, and C_6H_5 groups were present in place

238

$$\left[\left(\begin{array}{c} OCH_2CF_3 \\ -N{=}P- \\ OCH_2CF_3 \end{array}\right)_2 \left(\begin{array}{c} R \\ -N{=}P- \\ CH_2SiMe_3 \end{array}\right)\right]_n$$

CF_3CH_2ONa, CF_3CH_2OH
toluene, 110°C

$$\begin{array}{c} R \quad CH_2SiMe_3 \\ N{=}P{-}N \\ Cl{-}P \quad P{-}Cl \\ Cl \quad N \quad Cl \end{array} \xrightarrow{210°C} \left[\left(\begin{array}{c} Cl \\ -N{=}P- \\ Cl \end{array}\right)_2 \left(\begin{array}{c} R \\ -N{=}P- \\ CH_2SiMe_3 \end{array}\right)\right]_n$$

R = CH_3
C_2H_5
n-C_4H_9
C_6H_5

CF_3CH_2ONa, CF_3CH_2OH
THF, 66°C

$$\left[\left(\begin{array}{c} OCH_2CF_3 \\ -N{=}P- \\ OCH_2CF_3 \end{array}\right)_2 \left(\begin{array}{c} R \\ -N{=}P- \\ CH_3 \end{array}\right)\right]_n$$

Scheme 4

of the methyl group [5]. In all these systems, the organosilicon group remained attached to its anchoring phosphorus atom during the polymerization process.

The macromolecules isolated from polymerization of the type shown in Scheme 4 were treated with sodium trifluoroethoxide to remove the chlorine atoms and stabilize the molecules against hydrolysis. As with the cyclic trimers, phosphorus–chlorine and carbon–silicon bond cleavage occurred rapidly in tetrahydrofuran at 66°C. However, P–Cl bond cleavage was the predominant reaction in toluene at 110°C. The final silylphosphazene polymers were stable, non-crystalline, high molecular weight ($M_n = 10^5$–10^6) elastomers with low glass transition temperatures (-40 to $-60°$C). The ratio of NPR_2 to $NP(OCH_2CF_3)_2$ repeating units was estimated by ^{31}P NMR spectroscopy to be approximately $1/2$. The composition was confirmed by elemental microanalysis which also provided evidence that less than 1% of the chlorine atoms remained after the reaction with sodium trifluoroethoxide. In appearance, the polymers resemble silicone rubber, even though they are not crosslinked. Their properties as membranes and biocompatible materials are being investigated.

The polymerization of organosilylcyclophosphazenes provides one of two alternative routes to the synthesis of phosphazene polymers with organosilicon side groups. The other method, reported recently by Wisian–Neilson, Neilson, and coworkers [6], makes use of a metallation of alkyl groups attached to a preformed methyl/phenylphosphazene high polymer, followed by treatment with an organosilyl halide. The two methods are complementary in the sense that cosubstituent alkoxy, aryloxy, or amino side groups cannot be incorporated via the second method, while polymers that bear only alkyl or aryl units linked to the skeleton through phosphorus–carbon bonds have not yet been prepared by the first route.

Acknowledgements

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