Synthesis and Molecular Structure of Methylsilane- and Methylsiloxane-Cyclotriphosphazenes[1]

Harry R. Allcock,* David J. Brennan, James M. Graaskamp, and Masood Parvez

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

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(Methylsilyl)- and (methylsiloxy)chlorocyclotriphosphazenes of formula $N_3P_3Cl_5R$ (**1**), *gem*-$N_3P_3Cl_4R_2$ (**2**), and *gem*-$N_3P_3Cl_4(Me)R$ (**3**) have been synthesized, where R = $-CH_2SiMe_3$, $-CH_2SiMe_2OSiMe_3$, or $-CH_2\overline{Si(Me)-(OSiMe_2)_3-O}$. Compounds **1** and **2** are formed by the reactions of RMgCl with $(NPCl_2)_3$ in THF at 66 °C. Species **3** were prepared either by the reaction of **1** with MeMgCl in THF at 25 °C or by the reaction of $(NPCl_2)_3$ with MeMgCl/$[(n\text{-}Bu)_3PCuI]_4$ at -78 °C, followed by the addition of RI. The chlorine atoms in **1**–**3** could be replaced by trifluoroethoxy groups in the presence of sodium trifluoroethoxide. Cleavage of the PCH_2–Si bond by sodium trifluoroethoxide also occurred under certain reaction conditions, especially when R was $-CH_2\overline{Si(Me)-(OSiMe_2)_3-O}$. The mechanisms of these reactions are discussed. The crystal and molecular structures of **1**, **2**, and **3**, where R = $-CH_2\overline{Si(Me)-(OSiMe_2)_3-O}$, have been investigated by single-crystal X-ray diffraction. The phosphazene rings are puckered and have a nonsymmetric inequality of the skeletal bonds. Crystals of **2c** are triclinic with space group $P\bar{1}$, with a = 11.002 (4) Å, *b* = 15.148 (3) Å, *c* = 15.315 (3) Å, α = 117.71 (1)°, β = 97.36 (1)°, and γ = 96.33 (1)°, with *V* = 2198.6 Å^3 and *Z* = 2. Crystals of **3c** are monoclinic with space group $P2_1/c$, with a = 14.847 (2) Å, *b* = 8.620 (2) Å, *c* = 22.828 (3) Å, β = 100.59 (1)°, with *V* = 2871.8 Å^3 and *Z* = 4. Crystals of **1c** were isomorphous with those of **3c**.

Poly(organophosphazenes)[2-9] and poly(organosiloxanes)[10] constitute two of the best studied classes of inorganic backbone macromolecules. Each of these polymer systems has specific chemical and physical property characteristics that depend on the elements in the main chain and on the side groups attached to that chain.

Poly(organosiloxanes) are important because of the inherent flexibility of the siloxane chain and the hydrophobicity and thermooxidative stability associated with the presence of alkyl- or aryl- groups linked to the silicon atoms. On the other hand, because of the equilibration-type synthesis method used for poly(organosiloxanes), only a limited number of different side groups can be incorporated into these molecules.[11] The characteristics of poly(organophosphazenes) stem also from the high torsional flexibility of the backbone, mediated by the steric and polar characteristics of the side groups. However, the most important feature of poly(organophosphazene) chemistry is the ease with which different organic or organometallic side groups can be attached to the backbone. This is a consequence of the substitutive mode of assembly used for these polymers.[2-9]

The work described in this paper forms part of a program to synthesize macromolecules that combine the characteristics of poly(organophosphazenes) with those of organosilicon-based polymers. Specifically, we are concerned here with the development of methods for the linkage of organosilicon side groups to a phosphazene skeleton.

As in previous studies from our laboratory,[12] the first objective was to develop the chemistry at the small-molecule cyclotri- or cyclotetraphosphazene level. Subsequent studies will explore the polymerization of these species[7,13] and the extension of the same side group linkage reactions to phosphazene high polymers.

In principle, a number of different methods can be envisaged for the linkage of organosilicon units to a phosphazene ring or chain. The most obvious of these would involve the reaction of a triorganosiloxide anion, R_3SiO^-, with a halogenophosphazene, $(NPCl_2)_{3,4...n}$ or $(NPF_2)_{3,4...n}$, to yield species of type $[NP(OSiR_3)_2]_{3,4...n}$. Our experience with this type of reaction,[14] and reports of similar studies by Soviet workers,[15,16] indicate that such compounds are hydrolytically unstable, a consequence of the ease of cleavage of P–O–Si bonds in the presence of moisture.[17]

For this reason, we have focused on the synthesis of cyclophosphazenes in which the organosilicon side group is linked to the skeleton through carbon–phosphorus bonds. Such bonds are expected to be hydrolytically and thermally stable.

Results and Discussion

General Synthetic Approach. In earlier studies, we and others have developed a number of procedures for the linkage of alkyl or aryl groups to phosphazenes through the formation of phosphorus–carbon bonds.[18-31] These

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[1] This is the second paper from our laboratory on the reactions between phosphazenes and organosilicon compounds. For the first paper, see ref 14.

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

[3] Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

[4] Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.

[5] Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972: (a) Chapters 15 and 16; (b) Appendix I.

[6] Allcock, H. R. *Sci. Prog.* (*Oxford*) **1980**, *66*, 355.

[7] Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.

[8] Tate, D. P. *J. Polym. Sci., Polym. Symp.* **1974**, *48*, 33.

[9] Singler, R. E.; Hagnauer, G. L.; Sicka, R. W. *ACS Symp. Ser.* **1984**, *No. 260*, p 143.

[10] Hardman, B. B.; Torkelson, A. *Kirk-Othmer Encycl. Chem. Technol. 3rd. ed.* **1982**, *20*, 922.

[11] Allcock, H. R. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *C4*(2), 149.

[12] Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.

[13] Allcock, H. R. *Polymer* **1980**, *21*, 673.

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

[15] Belykh, S. I.; Zhivukhin, S. M.; Kireev, V. V.; Kolesnikov, G. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1969**, *14*, 668.

[16] Zhivukhin, S. M.; Tolstoguzov, V. B.; Ivanov, A. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1962**, *7*, 1134.

[17] Borisov, S. N.; Voronkov, M. G.; Lukevits, E. Ya. *Organosilicon Derivatives of Phosphorus and Sulfur*, Plenum Press: New York-London, 1971, Chapter 1.

[18] For a general review of the organometallic chemistry of phosphazenes, see: Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron Rep.* **1986**, in press.

[19] Allen, C. W.; Moeller, T. *Inorg. Chem.* **1968**, *7*, 2177.

[20] Oakley, R. T.; Rettig, S. J.; Paddock, N. L.; Trotter, J. *J. Am. Chem. Soc.* **1985**, *107*, 6923.

[21] Biddlestone, M.; Shaw, R. A. *J. Chem. Soc. A* **1969**, 178.

[22] Allcock, H. R.; Patterson, D. B.; Evans, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6095.

[23] Allcock, H. R.; Chu, C. T.-W. *Macromolecules* **1979**, *12*, 551.

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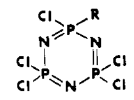
methods include the reactions of organometallic reagents, such as organolithium, organocopper, or Grignard reagents, with halogenophosphazenes, or the reactions of phosphazene anions with alkyl halides. In this paper, we describe an extension of this approach that allows the synthesis of (organosilyl)cyclotriphosphazenes of structures 1, 2, and 3. In addition, the reactions of species 1–3 with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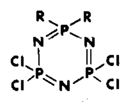
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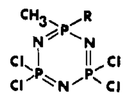
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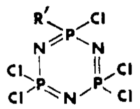
a, R = $-CH_2SiMe_3$ b, R = $-CH_2SiMe_2OSiMe_3$ c, R = $-CH_2Si(Me)-(OSiMe_2)_3-O$

sodium trifluoroethoxide have been examined. This reaction is important because, at the high polymeric level, the replacement of chlorine by alkoxy or aryloxy groups is necessary to generate hydrolytically stable macromolecules. As will be shown, these reactions are complicated by the removal of the organosilicon side groups by cleavage of the PCH_2–Si bond.

Two methods were used to prepare organosilicon derivatives 1–3. The first involved reaction of the Grignard reagents Me_3SiCH_2MgCl, $Me_3SiOSiMe_2CH_2MgCl$, or $O-(SiMe_2O)_3-Si(Me)CH_2MgCl$ with $(NPCl_2)_3$ to yield the monosubstituted compounds 1 and the geminal-disubstituted derivatives 2. Derivatives of type 3 were prepared by treatment of 1 with methylmagnesium chloride. The second method made use of the reaction between an anionic metallophosphazene intermediate and electrophiles such as ICH_2SiMe_3, $ICH_2SiMe_2OSiMe_3$, or $ICH_2Si(Me)-(OSiMe_2)_3-O$. These reactions yielded products of type 3. The two approaches will be discussed separately.

Reactions of Organosilyl Grignard Reagents with $(NPCl_2)_3$. It is known from earlier work that conventional alkyl or aryl Grignard reagents react with $(NPCl_2)_3$ in tetrahydrofuran to yield two main types of products, shown in 4 and 5. The type of Grignard reagent employed determines whether 4 or 5 is the favored product.[32] For example, when MeMgCl or EtMgCl are used, mixtures of 4 and 5 are formed. Bulkier Grignard reagents, such *t*-BuMgCl or *i*-PrMgCl, yield 4 exclusively. Phenylmagnesium chloride gives only 5.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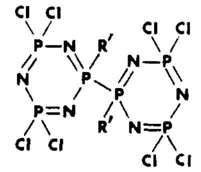
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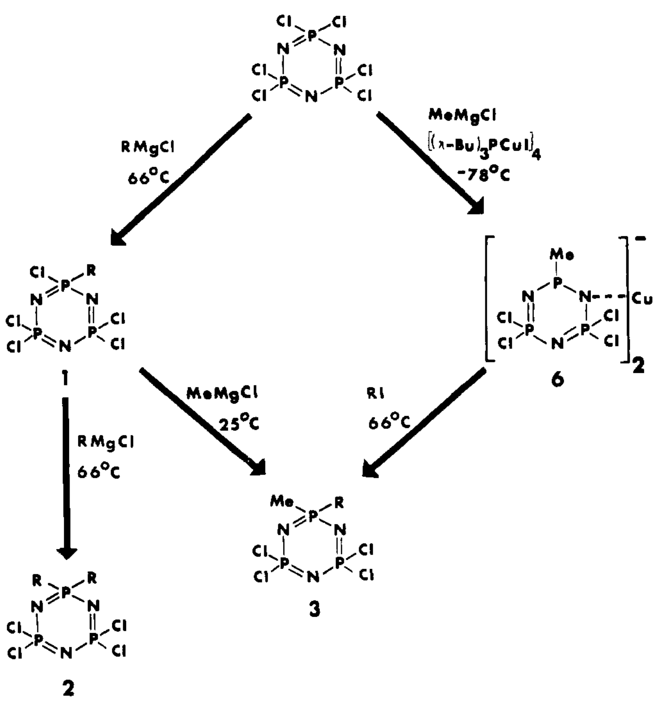
R′ = alkyl or aryl

Scheme I



R = $-CH_2SiMe_3$
$-CH_2SiMe_2OSiMe_3$
$-CH_2Si(Me)-(OSiMe_2)_3-O$

The organosilyl Grignard reagents Me_3SiCH_2MgCl, $Me_3SiOSiMe_2CH_2MgCl$, or $O-(SiMe_2O)_3Si(Me)CH_2MgCl$ react with $(NPCl_2)_3$ in tetrahydrofuran at 66 °C to give species corresponding to 4 (i.e., compounds 1) and compounds 2 in 50–80% yields (Scheme I). No evidence was found for the formation of bi(cyclotriphosphazenes) of type 5.

Whether the monosubstituted (1) or gem-disubstituted (2) products were formed depended on the reaction conditions and on the type of Grignard reagent. The interaction of equimolar equivalents of the Grignard reagent with $(NPCl_2)_3$ at 66 °C led, as might be expected, to the formation of 1 as the main product. In the presence of excess Grignard reagent at 66 °C, the geminal-disubstituted species 2 is the main product. Species 1 was detected as an intermediate. Pure 1 also reacts with RMgCl to give 2. However, replacement of the remaining four chlorine atoms in 2 was exceedingly difficult. Species 2 underwent no further reaction with the three Grignard reagents during 24 h at 66 °C.

At a lower temperature (25 °C), the main products from the reaction were the monosubstituted species 1 irrespective of the Grignard reagent used or the presence of excess Grignard. In the case of $O-(SiMe_2O)_3Si(Me)-CH_2MgCl$, the reaction was exceedingly slow, and good yields of 1 could be obtained only at 66 °C.

The reactions of MeMgCl with 1 to give 3 in 60–70% yield were accomplished under mild conditions (25 °C) and in the absence of excess Grignard reagent. However, species 3 did not react further with MeMgCl when an excess of this reagent was added.

Reactions of Phosphazene Anions with Organosilyl Electrophiles. The alternative route to compounds 3 was

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(24) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.
(25) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844.
(26) Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 2256.
(27) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.
(28) Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350.
(29) Allcock, H. R.; Connolly, M. S.; Harris, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 2482.
(30) Allcock, H. R.; Desorcie, J. L.; Wagner, L. J. *Inorg. Chem.* **1985**, *24*, 333.
(31) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337.
(32) Allcock, H. R.; Desorcie, J. L.; Harris, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 2814.

by reaction of a cyclotriphosphazene anion with an (iodomethylene)silane or (iodomethylene)siloxanes (Scheme I). We have shown in the past that $(NPCl_2)_3$ reacts with alkyl Grignard reagents in the presence of $[(n\text{-Bu})_3PCuI]_4$ at −78 °C to give a copper–phosphazene intermediate analogous to **6**.[24,25] This can be converted to dialkylcyclotriphosphazenes or alkylhydridophosphazenes by treatment with alkyl halides or 2-propanol, respectively.

In the present work, intermediate **6** (prepared from $(NPCl_2)_3$ and MeMgCl at −78 °C in the presence of $[(n\text{-Bu})_3PCuI]_4$) was allowed to react with ICH_2SiMe_3, $ICH_2SiMe_2OSiMe_3$, or $ICH_2\overline{Si(Me)\text{–}(OSiMe_2)_3\text{–}O}$ at 66 °C to give the three compounds of structure **3**. The yields of **3** via this route were lower (35–64%) than those obtained by the reactions of **1** with MeMgCl.

In the earlier work we showed that methyl iodide, allyl bromide, and propargyl bromide react with **6** even at 25 °C,[26,27] but ethyl iodide, *n*-propyl iodide, and *n*-butyl iodide did not. Thus, it is of interest to compare the reactivities of the organosilyl iodides with those of the simple organic iodides. The reactions of the organosilyl iodides with **6** proceeded efficiently only at temperatures near 66 °C. At 25 °C, $ICH_2\overline{Si(Me)\text{–}(OSiMe_2)_3\text{–}O}$ did not react with **6** during 72 h, but it reacted completely within 18 h at 66 °C. The reaction between **6** and ICH_2SiMe_3 was only 50% complete after 72 h at 25 °C but took place rapidly at 66 °C. The reactivity of $ICH_2SiMe_2OSiMe_3$ was intermediate between those of the other two reagents.

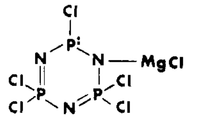
Silicon atoms adjacent to halomethyl groups activate these groups strongly to nucleophilic attack. For example, Me_3SiCH_2Cl reacts with iodide ion,[33] but Me_3CCH_2Cl does not.[34] Moreover, Me_3SiCH_2Cl reacts 20–30 times faster with iodide ion than does *n*-BuCl.[33] Similarly, Me_3SiCH_2I reacts slowly with **6** at 25 °C, but *n*-BuI does not react.

Steric effects must also play a role in these reactions. The lower reactivity of $\overline{O\text{–}(SiMe_2O)_3Si}(Me)CH_2I$ with **6**, compared to Me_3SiCH_2I, probably reflects a steric retardation. A similar trend in reactivity has been reported for the reactions of Me_3SiCH_2Cl, $Me_3SiOSiMe_2CH_2Cl$, and $\overline{O\text{–}(SiMe_2O)_3Si}(Me)CH_2Cl$ with iodide ion: Me_3SiCH_2Cl reacts fastest, while $\overline{O\text{–}(SiMe_2O)_3Si}(Me)CH_2Cl$ reacts slowest.[33]

Mechanism of the Reactions between Organosilyl Grignard Reagents and $(NPCl_2)_3$. The available evidence is compatible with the view that the organosilyl Grignard reagents react with $(NPCl_2)_3$ or with **1** by a nucleophilic halogen-replacement mechanism and not by a process that involves metal–halogen exchange. In this sense, these reactions follow a different mechanism from those between $(NPCl_2)_3$ and conventional alkyl or aryl Grignard reagents.[32]

The following evidence supports a direct nucleophilic substitution mechanism. First, no bi(cyclotriphosphazenes) of type **5** were detected from these organosilyl Grignard reactions. Bi(cyclophosphazenes) are formed in substantial yields when MeMgCl, EtMgCl, *n*-PrMgCl, or *n*-BuMgCl react with $(NPCl_2)_3$, and this is a key item of evidence for metal–halogen exchange reactions in these systems.[32] However, this evidence does not totally exclude a metal–halogen exchange mechanism in the organosilyl Grignard systems, because earlier work has shown that *i*-PrMgCl and *t*-BuMgCl react with $(NPCl_2)_3$ via a metal–halogen exchange reaction but do not yield bi(cyclotriphosphazenes).[32] Steric effects associated with the bulky alkyl groups appear to retard phosphazene ring-coupling reactions. Thus, it could be argued that even the Me_3SiCH_2– group is too bulky to allow bi(cyclotriphosphazene) formation.

A second piece of evidence against a metal–halogen exchange mechanism with the organosilyl Grignard reagents has been obtained from an attempt to trap intermediates formed in the reaction between Me_3SiCH_2MgCl and $(NPCl_2)_3$. This reaction was carried out in the presence of methyl iodide in tetrahydrofuran solvent. If a metal–halogen exchange mechanism can take place, intermediates such as **7** or **8** should be present in the reaction mixture,



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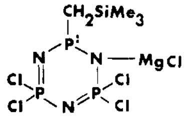

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and compounds such as $N_3P_3Cl_5Me$ or *gem*-$N_3P_3Cl_4(Me)(CH_2SiMe_3)$ would be the expected products from the interaction of **7** or **8** with methyl iodide. Such species were not detected.

Reactions of (Organosilyl)phosphazenes with Sodium Trifluoroethoxide. Compounds **1**–**3** react with sodium trifluoroethoxide to yield two types of products. First, the chlorine atoms are replaced by trifluoroethoxy groups to yield products such as **9**, **11**, or **13** (Scheme II) in which the organosilyl side groups retain their integrity. Second, PCH_2–Si bond cleavage can occur under the influence of sodium trifluoroethoxide to give products with methyl groups remaining in place of the organosilyl units. Carbon–silicon bond cleavage by alkoxides is a well-known process in organosilicon chemistry.[35] Cleavage of the PCH_2–Si bond can be controlled by the choice of reaction conditions.

Halogen replacement without carbon–silicon bond cleavage can be brought about by the use of a nonpolar solvent, such as toluene. For example, species **1**, **2**, or **3** (where R = $-CH_2SiMe_3$ or $-CH_2SiMe_2OSiMe_3$) reacted with an excess of sodium trifluoroethoxide (1.5 equiv/P–Cl bond) in toluene at 110 °C for 1–72 h (see Experimental Section for details) to yield the (organosilyl)(trifluoroethoxy)phosphazenes **9**, **11**, or **13**.

However, under the same conditions, species **1**, **2**, or **3** bearing $-CH_2\overline{Si(Me)\text{–}(OSiMe_2)_3\text{–}O}$ side groups underwent PCH_2–Si and Si–O bond cleavage as well as partial replacement of halogen by trifluoroethoxide. The use of dioxane as a solvent at 25 °C allowed replacement of the chlorine atoms by trifluoroethoxy groups and minimized, but did not eliminate, PCH_2–Si and Si–O bond cleavage. However, the use of tetrahydrofuran as a solvent at 25 °C resulted in cleavage of all the PCH_2–Si bonds. All three compounds (**1**–**3**) underwent facile PCH_2Si bond cleavage in tetrahydrofuran at 66 °C to give products such as **10** or **12**. Species **10** has been prepared previously by another route.[36]

A phosphazene ring can be viewed as an electron-withdrawing group that activates a nearby carbon–silicon bond to cleavage, especially when chloro or trifluoroethoxy cosubstituent groups are present. Such cleavage would be less facile in a nonpolar solvent, such as toluene, and highest in a more polar solvent, such as tetrahydrofuran.

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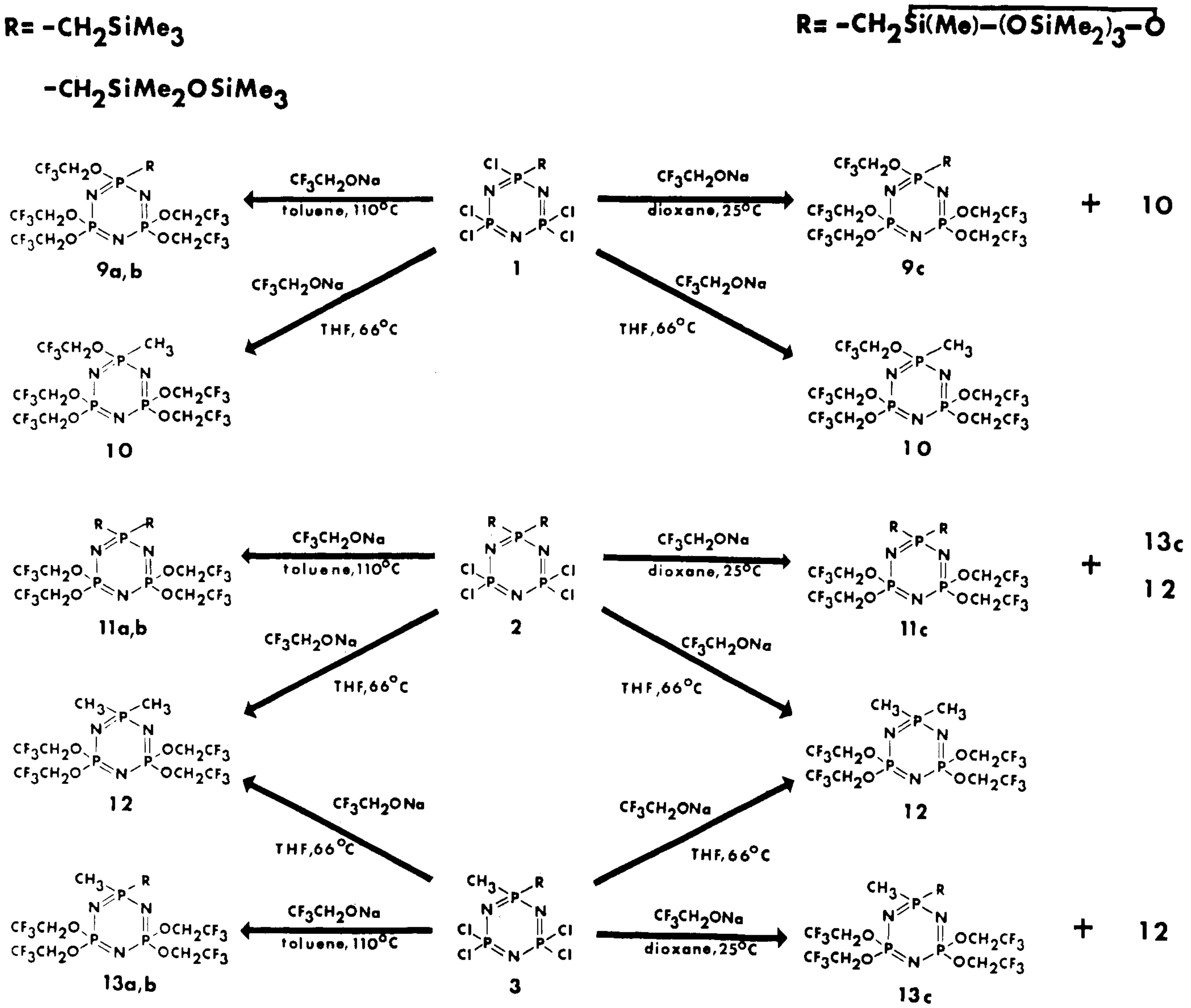
(33) Cooper, G. D.; Prober, M. *J. Am. Chem. Soc.* **1954**, *76*, 3943.

(34) Whitmore, F. C.; Fleming, G. H.; *J. Am. Chem. Soc.* **1933**, *55*, 4161.

(35) Roedel, G. F. *J. Am. Chem. Soc.* **1949**, *71*, 269.

(36) Allcock, H. R.; Ritchie, R. J.; Harris, P. J. *Macromolecules* **1980**, *13*, 1332.

Scheme II



Carbon–silicon bond cleavage was enhanced in toluene when the phase-transfer catalyst $(n\text{-Bu})_4NBr$ was present.

The marked susceptibility of species with $-\overline{CH_2Si(Me)-(OSiMe_2)_3-O}$ side groups to undergo carbon–silicon bond cleavage in all three solvents, and at 25 °C as well as 66 °C, may be due to the increased electropositive character of the silicon atom as a consequence of the presence of two neighboring oxygen atoms. However, it is clear from these results that, in the projected transfer of this chemistry to the phosphazene high polymer level, the cyclotetrasiloxane side group would be an inappropriate substituent if the final step in the synthesis involved reactions with sodium trifluoroethoxide or similar nucleophiles.

Structural Characterization of 1–3 and 9–13. These compounds were characterized by a combination of ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, infrared spectroscopy, mass spectrometry, and microanalysis.

Microanalytical data are presented in Table I and are consistent with the proposed structures. The mass spectra for all the cyclotriphosphazenes showed the expected parent ion peak. Major fragments were detected for the loss of methyl (M − 15) from each compound, and loss of chlorine (M − 35) (compounds **1–3**). The correct chlorine isotope pattern was detected when applicable.

The ^{31}P NMR spectra (Table II) of the cyclotriphosphazenes were consistent with the expected distribution of substituents around the phosphazene ring. An AB_2 spin pattern was found for the chlorocyclotriphosphazenes, with the P(C)(Cl) or $P(C)_2$ resonances at 42–36 ppm and the PCl_2 shifts at 21–14 ppm. Little or no coupling was detected (J_{PNP} = 0–8 Hz). The ^{31}P NMR spectra for the (trifluoroethoxy)cyclotriphosphazenes were also AB_2 spin systems, with the P(C)(O) and $P(C)_2$ resonance at 43–38 ppm (triplet) and the $P(O)_2$ resonance at 16–13 ppm (doublet).

The ^{1}H NMR spectra (Table III) of the methylsilane and methylsiloxane substituted chloro- and (trifluoroethoxy)cyclotriphosphazenes showed resonances for $SiCH_3$ at δ 0.4–0.0 (singlet), PCH_2Si and PCH_3 at δ 2.0–1.2 (doublet or doublet of triplets), and OCH_2CF_3 at δ 4.3–4.0 (multiplet).

The ^{13}C NMR spectra (Table III) of these same compounds contained resonances for $SiCH_3$ at 2.2 to −0.6 ppm (singlet or doublet), PCH_2Si and PCH_3 at 31–21 ppm (doublet or doublet of triplets), OCH_2CF_3 at 63–60 ppm (quartet), and OCH_2CF_3 at 127–122 ppm (quartet of triplets).

The infrared spectra were consistent with the proposed structures. Characteristic vibrations for P–N (1250–1150 cm^{-1}), P–O (970 cm^{-1}), P–Cl (600–580, 520–500 cm^{-1}),

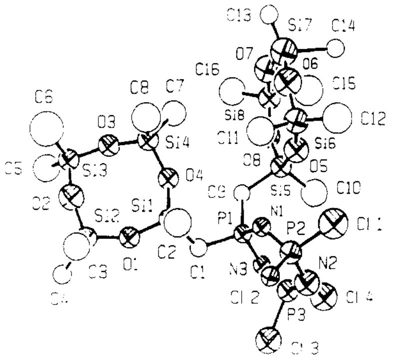


Figure 1. Structure of 2c.

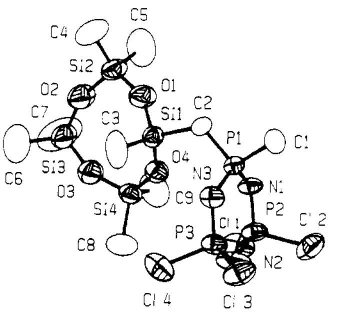
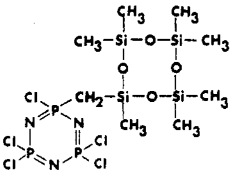


Figure 2. Structure of 3c.

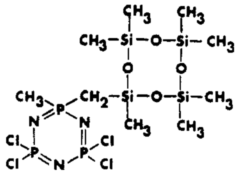
Si-O-Si (1090–1040 cm^{-1}), Si-CH_3 (1260–1250, 850–800 cm^{-1}), and C–H (2980–2960 cm^{-1}) were detected.

Additional characterization was provided by two X-ray structure studies.

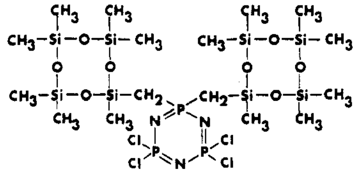
Crystal and Molecular Structures of 1c, 2c, and 3c. Compounds **1c**, **2c**, and **3c** were examined by single-crystal X-ray diffraction techniques. Many cyclotriphosphazenes have been examined by X-ray crystallography,[5b,18,37] and the structures of several cyclotetrasiloxanes have been reported.[38-47] Other compounds have been prepared in which cyclotriphosphazene and cyclotetrasiloxane rings have been linked together by P-$NH(CH_2)_3$-Si units.[48] The structure of one of them, $N_3P_3(NMe_2)_5NH(CH_2)_3\overline{Si(Me)(OSiMe_2)_3O}$, has been examined by X-ray crystallography.[49]



1c



3c



2c

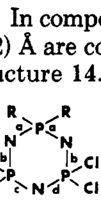
Specific questions that we wished to answer are as follows. (1) What effect does a cyclotetrasiloxane ring have on the bond lengths, bond angles, and planarity of a phosphazene ring? (2) How does a cyclotriphosphazene ring affect the structural parameters, especially the ring conformation, of a cyclotetrasiloxane ring? (3) What are the structural differences between the component rings in **1c**, **2c**, and **3c** and their counterparts in other alkylchlorocyclotriphosphazenes, methylcyclosiloxanes, or $N_3P_3(NMe_2)_5NH(CH_2)_3\overline{Si(Me)(OSiMe_2)_3O}$?

The initial data set collected for **1c** revealed that the crystals were isomorphous with those derived from **3c**. Thus, the structure of **1c** was not solved further. The structures of **2c** and **3c** are shown in Figures 1 and 2, respectively. Bond lengths (Tables IV and V), bond angles (Tables VI and VII), and positional parameters (Tables VIII and IX) for **2c** and **3c** are also given.

Compound **2c** consists of a cyclic trimeric phosphazene ring, with two cyclotetrasiloxane rings attached geminally, through P-CH_2-Si linkages, to P(1). Two chlorine atoms are bonded to each of the two remaining phosphorus atoms. Two methyl groups are attached to each silicon atom in the cyclotetrasiloxane rings except at the silicon atoms that are part of the P-CH_2-Si ring linkage unit. These two silicon atoms contain one methyl group and one methylene unit. Compound **3c** is similar to **2c** except that a methyl group is present in place of one heptamethylmethylenecyclotetrasiloxane unit at P(1).

The phosphazene ring in **2c** is slightly puckered (χ^2 = 844 for the weighted least-squares plane through the phosphazene ring).[50] A plane passes through atoms P(1), P(2), P(3), N(1), and N(2) (χ^2 = 130), while atom N(3) deviates from this plant by 0.167 (9) Å. In **3c**, the phosphazene ring is more puckered (χ^2 = 3007). Atoms P(1) and N(1) deviate from the least-squares plane through P(2), P(3), N(2), and N(3) (χ^2 = 413) by −0.055 (1) and 0.110 (5) Å, respectively.

The P–N bond lengths in both **2c** and **3c** vary according to the distance from P(1). In compound **2c**, the two longest bonds (average = 1.623 (2) Å are connected to P(1) [bonds PN(a)], as shown in structure **14**. The bond distances, PN(b), between N(1)–P(2) and N(3)–P(3), are similar in



14

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[37] Bullen, G. J. *J. Chem. Soc. A* **1971**, 1450.

[38] Hossain, M. A.; Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 522.

[39] Brago, D.; Zanotti, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 950.

[40] Shklover, V. E.; Kalinin, A. E.; Gusev, A. I.; Bokii, N. G.; Struchkov, Yu. T.; Andrianov, K. A.; Petrova, I. M. *J. Struct. Chem. (Engl. Transl.)* **1973**, *14*, 639.

[41] Steinfink, H.; Post, B.; Fankuchen, I. *Acta Crystallogr.* **1955**, *8*, 420.

[42] Carlstrom, D.; Falkenberg, G. *Acta Chem. Scand.* **1973**, *27*, 1203.

[43] Soderholm, M.; Carlstrom, D. *Acta Chem. Scand. Ser. B* **1977**, *B31*, 193.

[44] Soderholm, M. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 171.

[45] Shklover, V. E.; Dubchak, I. L.; Struchkov, Yu. T.; Khynku, E. S.; Zhdanov, A. A. *J. Struct. Chem. (Engl. Transl.)* **1981**, *22*, 229.

[46] Shklover, V. E.; Dubchak, I. L.; Struchkov, Yu. T.; Mileshkevich, V. P.; Nikolaev, G. A.; Tsyganov, Yu. V. *J. Struct. Chem. (Engl. Transl.)* **1981**, *22*, 225.

[47] Dubchak, I. L.; Shklover, V. E.; Struchkov, Yu. T.; Khynku, E. S.; Zhdanov, A. A. *J. Struct. Chem. (Engl. Transl.)* **1981**, *22*, 770.

[48] Kireev, V. V.; Kovyazin, V. A.; Kopylov, V. M.; Zaitseva, M. G.; Mitropol'skaya, G. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 1692.

[49] Ovchinnikov, Yu. E.; Shklover, V. E.; Struchkov, Yu. T.; Remizova, A. A.; Kopylov, V. M.; Kovyazin, V. A.; Kireyev, V. V. *Z. Anorg. Allg. Chem.* **1985**, *523*, 14.

[50] Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination*; The MacMillan Co.: London, 1968; pp. 421–425.

Table I. Characterization Data

compd	mp, °C	% yield	mass spectral data found	mass spectral data calcd	elemental anal.	elemental anal. found	elemental anal. calcd
$N_3P_3Cl_5CH_2SiMe_3$ (**1a**)	58–59	82	399[a]	399	C	12.04	12.03
					H	2.88	2.78
					N	10.48	10.52
$N_3P_3Cl_5CH_2SiMe_2OSiMe_3$ (**1b**)	oil	67	473[a]	473	C	15.48	15.22
					H	3.68	3.63
					N	8.77	8.87
$N_3P_3Cl_5CH_2\overline{Si(Me)(OSiMe_2)_3O}$ (**1c**)	48–49	66	607[a]	607	C	15.74	15.81
					H	3.82	3.82
					N	6.78	6.91
gem-$N_3P_3Cl_4(CH_2SiMe_3)_2$ (**2a**)	103–104	62	451[b]	451	C	21.20	21.29
					H	4.88	4.92
					N	9.25	9.31
gem-$N_3P_3Cl_4(CH_2SiMe_2OSiMe_3)_2$ (**2b**)	oil	55	599[b]	599	C	24.42	24.04
					H	5.45	5.73
					N	7.17	7.01
gem-$N_3P_3Cl_4[CH_2\overline{Si(Me)(OSiMe_2)_3O}]_2$ (**2c**)	80–81	67	867[b]	867	C	22.13	22.14
					H	5.28	5.35
					N	4.77	4.84
gem-$N_3P_3Cl_4(Me)(CH_2SiMe_3)$ (**3a**)	114–115	69[c] (64[d])	379[b]	379	C	15.87	15.84
					H	3.62	3.73
					N	10.98	11.09
gem-$N_3P_3Cl_4(Me)(CH_2SiMe_2OSiMe_3)$ (**3b**)	58–59	67[c] (36)[d]	453[b]	453	C	18.19	18.55
					H	4.34	4.46
					N	9.31	9.27
gem-$N_3P_3Cl_4(Me)[CH_2\overline{Si(Me)(OSiMe_2)_3O}]$ (**3c**)	80–81	63[c] (39)[d]	587[b]	587	C	18.69	18.40
					H	4.38	4.47
					N	7.23	7.15
$N_3P_3(OCH_2CF_3)_5CH_2SiMe_3$ (**9a**)	oil	76	717	717	C	23.36	23.44
					H	3.03	2.96
					N	6.07	5.86
$N_3P_3(OCH_2CF_3)_5CH_2SiMe_2OSiMe_3$ (**9b**)	oil	59	791	791	C	24.30	24.27
					H	3.49	3.45
					N	5.28	5.31
$N_3P_3(OCH_2CF_3)_5[CH_2\overline{Si(Me)(OSiMe_2)_3O}]$ (**9c**)	oil	35	925	925	C	23.36	23.35
					H	3.62	3.60
					N	4.86	4.54
gem-$N_3P_3(OCH_2CF_3)_4(CH_2SiMe_3)_2$ (**11a**)	oil	59	705	705	C	26.94	27.23
					H	4.10	4.29
					N	6.05	5.96
gem-$N_3P_3(OCH_2CF_3)_4(CH_2SiMe_2OSiMe_3)_2$ (**11b**)	oil	49	853	853	C	28.04	28.13
					H	4.97	4.97
					N	5.10	4.92
gem-$N_3P_3(OCH_2CF_3)_4[CH_2\overline{Si(Me)(OSiMe_2)_3O}]_2$ (**11c**)	oil	8	1121	1121	C	25.81	25.68
					H	4.84	4.86
					N	4.09	3.74
gem-$N_3P_3(OCH_2CF_3)_4(Me)(CH_2SiMe_3)$ (**13a**)	25–26	73	633	633	C	24.77	24.64
					H	3.68	3.51
					N	6.74	6.64
gem-$N_3P_3(OCH_2CF_3)_4(Me)(CH_2SiMe_2OSiMe_3)$ (**13b**)	oil	71	707	707	C	25.73	25.46
					H	4.00	4.00
					N	6.27	5.94
gem-$N_3P_3(OCH_2CF_3)_4(Me)[CH_2\overline{Si(Me)(OSiMe_2)_3O}]$ (**13c**)	oil	51	841	841	C	24.27	24.25
					H	4.37	4.08
					N	5.32	4.99
gem-$N_3P_3(OCH_2CF_3)_4Me_2$ (**12**)	40	73	561	561	C	21.68	21.40
					H	2.59	2.52
					N	7.73	7.49

[a] Cl_5 isotope pattern. [b] Cl_4 isotope pattern. [c] Method a (see Experimental Section). [d] Method b (see Experimental Section).

length, with an average distance of 1.551 (1) Å. This pattern of long skeletal bonds flanking the heterosubstitution site, followed by short bonds [PN(b)] is common to many cyclotriphosphazenes.[51-56] The normal pattern is for the symmetrically disposed bonds, PN(c) and PN(d), to be equal to each other in length and intermediate between those of PN(a) and PN(b). This pattern is not found for **2c**. The two PN bonds distal from the cyclo-

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(51) Allcock, H. R.; Connolly, M. S.; Whittle, R. R. *Organometallics* **1983**, *2*, 1514.

(52) Whittle, R. R.; Desorcie, J. L.; Allcock, H. R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 546.

(53) Allcock, H. R.; Suszko, P. R.; Wagner, L. J.; Whittle, R. R.; Boso, B. *Organometallics* **1985**, *4*, 446 and references cited therein.

(54) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Inorg. Chem.* **1980**, *19*, 2483.

(55) Mani, N. V.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1965**, *19*, 693.

(56) Allcock, H. R.; Wagner, L. J.; Levin, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 1321.

Table II. ^{31}P **NMR Data**[a]

compd	signal	chem shift, ppm	coupling const, Hz
$N_3P_3Cl_5CH_2SiMe_3$ (**1a**)	$P(Cl)_2$	20.6	J_{PNP} = unresolved
	P(Cl)(C)	42.0	
$N_3P_3Cl_5CH_2SiMe_2OSiMe_3$ (**1b**)	$P(Cl)_2$	20.7	J_{PNP} = unresolved
	P(Cl)(C)	40.8	
$N_3P_3Cl_5CH_2\overline{Si(Me)(OSiMe_2)_3O}$ (**1c**)	$P(Cl)_2$	20.6	J_{PNP} = 5.8
	P(Cl)(C)	40.1	
gem-$N_3P_3Cl_4(CH_2SiMe_3)_2$ (**2a**)	$P(Cl)_2$	15.5	J_{PNP} = unresolved
	$P(C)_2$	40.3	
gem-$N_3P_3Cl_4(CH_2SiMe_2OSiMe_3)_2$ (**2b**)	$P(Cl)_2$	15.5	J_{PNP} = 6.1
	$P(C)_2$	38.2	
gem-$N_3P_3Cl_4[CH_2\overline{Si(Me)(OSiMe_2)_3O}]_2$ (**2c**)	$P(Cl)_2$	15.7	J_{PNP} = 7.7
	$P(C)_2$	36.7	
gem-$N_3P_3Cl_4(Me)(CH_2SiMe_3)$ (**3a**)	$P(Cl)_2$	16.9	J_{PNP} = 6.8
	$P(C)_2$	38.0	
gem-$N_3P_3Cl_4(Me)(CH_2SiMe_2OSiMe_3)$ (**3b**)	$P(Cl)_2$	16.6	J_{PNP} = 7.4
	$P(C)_2$	37.1	
gem-$N_3P_3Cl_4(Me)[CH_2\overline{Si(Me)(OSiMe_2)_3O}]$ (**3c**)	$P(Cl)_2$	16.9	J_{PNP} = 8.3
	$P(C)_2$	36.3	
$N_3P_3(OCH_2CF_3)_5CH_2SiMe_3$ (**9a**)	$P(O)_2$	15.5	J_{PNP} = 45.6
	P(O)(C)	43.2	
$N_3P_3(OCH_2CF_3)_5CH_2SiMe_2OSiMe_3$ (**9b**)	$P(O)_2$	15.5	J_{PNP} = 46.2
	P(O)(C)	41.0	
$N_3P_3(OCH_2CF_3)_5[CH_2\overline{Si(Me)(OSiMe_2)_3O}]$ (**9c**)	$P(O)_2$	15.4	J_{PNP} = 46.9
	P(O)(C)	40.3	
gem-$N_3P_3(OCH_2CF_3)_4(CH_2SiMe_3)_2$ (**11a**)	$P(O)_2$	13.6	J_{PNP} = 29.3
	$P(C)_2$	41.8	
gem-$N_3P_3(OCH_2CF_3)_4(CH_2SiMe_2OSiMe_3)_2$ (**11b**)	$P(O)_2$	13.9	J_{PNP} = 29.9
	$P(C)_2$	39.5	
gem-$N_3P_3(OCH_2CF_3)_4[CH_2\overline{Si(Me)(OSiMe_2)_3O}]_2$ (**11c**)	$P(O)_2$	14.0	J_{PNP} = 30.9
	P(O)(C)	38.2	
gem-$N_3P_3(OCH_2CF_3)_4(Me)(CH_2SiMe_3)$ (**13a**)	$P(O)_2$	14.5	J_{PNP} = 29.9
	$P(C)_2$	39.6	
gem-$N_3P_3(OCH_2CF_3)_4(Me)(CH_2SiMe_2OSiMe_3)$ (**13b**)	$P(O)_2$	14.7	J_{PNP} = 30.2
	$P(C)_2$	38.7	
gem-$N_3P_3(OCH_2CF_3)_4(Me)[CH_2\overline{Si(Me)(OSiMe_2)_3O}]$ (**13c**)	$P(O)_2$	14.8	J_{PNP} = 31.3
	$P(C)_2$	38.0	
gem-$N_3P_3(OCH_2CF_3)_4(CH_3)_2$ (**12**)	$P(O)_2$	15.2	J_{PNP} = 30.7
	$P(C)_2$	37.5	

[a] $CDCl_3$ solution.

siloxane linkage site are markedly unequal in length. Bond P(2)–N(2) [PN(c)] has a length of 1.581 (5) Å, and P(3)–N(2) [PN(d)] is 1.539 (5) Å.

Compound **3c** also shows the same deviation from the normal pattern. In this compound, the longest average bond lengths are PN(a) = 1.625 (2) Å, while the shortest are PN(b) = 1.556 (2) Å. However, the P(2)–N(2) [PN(c)] bond distance of 1.587 (3) Å differs markedly from that of P(3)–N(2) [PN(d)], which is 1.558 (3) Å. Although steric effects might be invoked to explain these anomalies, it is curious that the phenomenon has not been detected earlier for a wide range of non-siloxane side groups.

The endocyclic bond angles of the cyclophosphazene rings in both **2c** and **3c** are distorted from the normal values, as required by the unequal bond lengths. A "normal" endocyclic angle at phosphorus is assumed to have the value of 118.4 (2)° found in $(NPCl_2)_3$.[37] The largest deviation from this angle is at P(1) in both **2c** and **3c**, where values of 113.7 (2)° and 114.0 (2)°, respectively, were found. This narrowing of the ring angle may reflect a response to a steric widening of the X–P–X exocyclic angle from 101.5 (2)° for $(NPCl_2)_3$[37] to 106.3 (3)° for **2c** and 105.5 (2)° for **3c**. These latter values are similar to the C–P–C angles found in alkyl- or arylcyclotriphosphazenes.[51]

The P–C bond lengths in **2c** and **3c** are normal when compared to other alkylphosphazenes.[51,52,54,55] Both P–C bonds in **2c** are similar in length [(P(1)–C(1) = 1.802 (5) Å and P(1)–C(9) = 1.789 (5) Å], but the P–CH_3 bond in **3c** of 1.808 (4) Å is slightly longer than the P–CH_2 value of 1.781 (4) Å. The P–Cl bond lengths in both **2c** and **3c** are similar, with average values of 1.997 (3) and 1.999 (4) Å, respectively. The average Cl–P–Cl bond angles are 100.0 (2)° for **2c** and 100.05 (2)° for **3c**, values that are similar to those found for $(NPCl_2)_3$[37] and other chlorocyclotriphosphazenes.[51,52,54]

The cyclosiloxane rings in **2c** and **3c** are puckered, as they are in all cyclosiloxane rings with more than three repeating units.[57] The siloxane rings in **2c** appear to adopt a slight boat-type conformation (ring A[62]) and a slight chair-type conformation (ring B[62]), while the siloxane ring in **3c** adopts a boat conformation. The ring conformations are illustrated by the stereoscopic views of **2c** and **3c** (Figures 3 and 4 in the supplementary material) and by the analysis of least-squares planes through the silicon atoms of the cyclosiloxane rings (Tables X and XI). The four silicon atoms in ring B of **2c** lie in a plane ($\chi^2 = 15$) as they do in $(OSiMe_2)_4$ which also adopts a chair con-

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(57) The cyclic trimeric siloxanes, such as $(OSiMe_2)_3$,[58] $(OSiPh_2)_3$,[59] and others,[60] are planar, while the cyclic tetramers[38–47] and cyclic octamer $(OSiMe_2)_8$[61] are puckered.

(58) Weller-Aggarwal, E. H.; Bauer, S. H. *J. Chem. Phys.* **1950**, *18*, 42.

(59) Bokii, N. G.; Zakharova, G. N.; Struchkov, Yu. T. *J. Struct. Chem.* (*Engl. Transl.*) **1972**, *13*, 267.

(60) Roth, W. L.; Harker, D. *Acta Crystallogr.* **1948**, *1*, 34.

(61) Frevel, L. K.; Hunter, M. J. *J. Am. Chem. Soc.* **1945**, *67*, 2275.

(62) Ring "A" is defined as the cyclotetrasiloxane ring that contains Si(1)–Si(4), while ring "B" is defined as the cyclotetrasiloxane ring that contains Si(5)–Si(8).

formation.[41] The silicon atoms in ring A of **2c** do not lie in a plane. The presence of both a boat and a chair conformation of the siloxane rings in **2c** may be due to steric interactions between rings A and B. The siloxane ring of **3c** is similar to $N_3P_3(NMe_2)_5NH(CH_2)_3Si(Me)(OSiMe_2)_3O$,[49] 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane,[42] and 1,1,2,2-tetramethyl-3,3,4,4-tetraphenylcyclotetrasiloxane[40] which also adopt boat conformations.

The structural parameters within the cyclosiloxane rings of **2c** and **3c** are similar to those found in $N_3P_3(NMe_2)_5NH(CH_2)_3Si(Me)(OSiMe_2)_3O$,[49] $(OSiMe_2)_4$,[41] $Me_6Ph_2O_4Si_4$,[42] and $Me_4Ph_4O_4Si_4$[40] (Table XII). The average Si–O bond distances in **2c** and **3c** were 1.61 (1) Å (ring A[62] of **2c**), 1.60 (3) Å (ring B[62] of **2c**), and 1.61 (1) Å (for **3c**). The average Si–C bond length in ring A of **2c** was 1.87 (3) Å, in ring B of **2c** was 1.84 (6) Å, and in **3c** was 1.85 (2) Å. The specific Si–CH_2P bond lengths were 1.902 (5) Å (ring A of **2c**), 1.883 (5) Å (ring B of **2c**), and 1.864 (4) Å (for **3c**). The high thermal motion of the carbon atoms in **2c** and **3c** caused variations in the individual bond lengths, but the average values did not differ appreciably from those in other systems.

The endocyclic O–Si–O and Si–O–Si bond angles, and the exocyclic C–Si–C angles in **2c** and **3c** are unexceptional. The average O–Si–O angles were 109.3 (3)°, 110 (1)°, and 108.8 (4) Å for rings A and B of **2c** and for **3c**, respectively. The near tetrahedral geometry of these angles is similar to the values for other cyclotetrasiloxanes shown in Table XII. The C–Si–C bond angles were also affected by the high thermal motion of the carbon atoms. However, the average values of 113 (1)°, 109 (6)°, and 112 (1)° for rings A and B of **2c** and for **3c**, respectively, are similar to reported values for related compounds (Table XII). The C–Si–C bond angles at the site of attachment to the phosphazene ring did not differ significantly from the other C–Si–C angles.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was kindly provided by the Firestone Tire and Rubber Co. and was purified by recrystallization from hexane and sublimation at 50 °C (0.05 mmHg). (Chloromethyl)trimethylsilane and (chloromethyl)pentamethyldisiloxane were obtained from Petrarch Systems, Inc., and were dried over molecular sieves before use. (Chloromethyl)heptamethylcyclotetrasiloxane was prepared by the method of Krieble and Elliot.[63] Octamethylcyclotetrasiloxane was obtained from Petrarch Systems Inc. and was used as received. (Iodomethyl)trimethylsilane, (iodomethyl)pentamethyldisiloxane, and (iodomethyl)heptamethylcyclotetrasiloxane were prepared by the reaction of the corresponding chloromethyl compound with sodium iodide in acetone[64-66] and were distilled before use. Trifluoroethanol (Halocarbon Products) was dried over 3-Å molecular sieves before use. Methylmagnesium chloride was obtained from Alfa Products as a 3.3 M solution in tetrahydrofuran and was used as received. The reagent, $[(n\text{-}Bu)_3PCuI]_4$, was prepared by standard methods.[67] Resublimed magnesium was obtained from Alfa Products and was used as received. Sodium hydride (Aldrich) was washed several times with dry THF to remove mineral oil and was stored in a drybox before use. Tetrahydrofuran (THF), 1,4-dioxane, and toluene were dried over sodium benzophenone ketyl and were distilled in an atmosphere of dry nitrogen before use. All reactions were carried out in an atmosphere of dry nitrogen.

Analytical Techniques. ^{31}P NMR (^1H-decoupled) spectra were obtained with a Varian CFT-20 NMR spectrometer operated at 32 MHz or a JEOL FX90Q NMR spectrometer operated at 36.2 MHz. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive shift values downfield from the reference. ^1H NMR spectra were recorded with the use of a Bruker WP-200 spectrometer operated at 200 MHz. Chemical shifts are relative to tetramethylsilane at δ 0. ^{13}C NMR (^1H-decoupled) spectra were recorded with the use of a Bruker WP-200 spectrometer operated at 50.3 MHz or a JEOL FX90Q spectrometer operated at 22.5 MHz. All spectra are referenced to internal tetramethylsilane at 0 ppm. Infrared spectra were obtained with the use of a Perkin-Elmer 283B grating spectrometer. The X-ray crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer controlled by a PDP 11/44 computer. The structures were solved by SDP[68] installed on the PDP 11/44. Preparative liquid chromatography was carried out with a Waters Associates Prep LC/System 500. Two Prep Pak-500/silica cartridges were used. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of $N_3P_3Cl_5R$ (1). Compounds **1a**, **1b**, and **1c** were prepared in an identical manner. (Chloromethyl)trimethylsilane, (chloromethyl)pentamethyldisiloxane, or (chloromethyl)heptamethylcyclotetrasiloxane (0.100 mol) was added dropwise to a stirred suspension of Mg (3.65 g, 0.150 mol) in dry THF (200 mL). (The Grignard reagent usually began to form during the first 15 min of halide addition; however, it was sometimes necessary to add ethylene dibromide (0.5–1 mL) and reflux the mixture at 66 °C to initiate the Grignard formation.) When the Grignard reaction had ceased, the solution was stirred at 66 °C for 3 h and then cooled to 25 °C. The Grignard solution was transferred via a double-tipped syringe needle to an addition funnel under nitrogen and was added dropwise to a solution of $(NPCl_2)_3$ (30.0 g, 0.0865 mol) in dry THF (500 mL) at 66 °C. On completion of addition, the reaction mixture was refluxed at 66 °C for 24 h. On cooling, THF was removed under reduced pressure, and diethyl ether (500 mL) was added to the residue. This mixture was washed with 3–250-mL portions of 5% aqueous HCl, and the ether layer was dried over $MgSO_4$. Suction filtration through Fuller's Earth yielded a clear solution from which the ether was removed under reduced pressure to yield an oil or solid. Preparative liquid chromatography, with use of a 10–20% CH_2Cl_2/80–90% hexane solvent mixture, was sometimes necessary to separate **1** from small amounts of impurities such as residual $(NPCl_2)_3$ or **2**. Crude products **1a** and **1c** were crystallized from dry ice/2-propanol–chilled pentane to yield white solids that sublimed at 60–100 °C (0.05 mmHg). Compound **1b** was an oil that was purified by distillation at 108 °C (0.05 mmHg). See Tables I–III for complete characterization data.

Synthesis of *gem*-$N_3P_3Cl_4R_2$ (2). Compounds **2a**, **2b**, and **2c** were prepared in an identical manner, using the following procedure. (Chloromethyl)trimethylsilane, (chloromethyl)pentamethyldisiloxane, or (chloromethyl)heptamethylcyclotetrasiloxane (0.210 mol) was added dropwise to a stirred suspension of Mg (7.30 g, 0.300 mol) in dry THF (400 mL). (At this point, the procedure described for the preparation of $N_3P_3Cl_5R$ (**1**) was followed exactly.) A crude product was isolated by removal of the ether under reduced pressure. Compound **2a** was recrystallized from hexane to yield a white solid that sublimed at 100–110 °C (0.05 mmHg). Compound **2b** was an oil that was first purified by preparative liquid chromatography using a 20% CH_2Cl_2/80% hexane solvent mixture, followed by distillation at 127 °C (0.05 mmHg). Compound **2c** was a solid that was crystallized from dry ice/2-propanol–chilled pentane and distilled at 165 °C (0.1 mmHg). See Tables I–III for complete characterization data.

Synthesis of *gem*-$N_3P_3Cl_4(Me)R$ (3). Compounds **3a**, **3b**, and **3c** were prepared by two methods. **Method a.** Compound **1** (0.0650 mol) was dissolved in dry THF (400 mL) and was stirred at 0 °C. Methylmagnesium chloride (39 mL of a 3.3 M solution

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[63] Krieble, R. H.; Elliott, J. R. *J. Am. Chem. Soc.* **1946**, *68*, 2291.
[64] Whitmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 481.
[65] Roedel, G. F. *J. Am. Chem. Soc.* **1949**, *71*, 269.
[66] Sommer, L. H.; Masterson, J. M.; Steward, O. W.; Leitheiser, R. H. *J. Am. Chem. Soc.* **1956**, *78*, 2010.
[67] Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 9.
[68] Structure Determination Package (SDP), B. A. Fritz and Associates, Inc., College Station, Texas 77840, and Enraf-Nonius, Delft, Holland, 1982.

Table III. ^{1}H and ^{13}C NMR Data[a]

compd	signal	^{1}H NMR,[b] δ	^{13}C NMR,[b] ppm	coupling const, Hz	
$\mathrm{N_3P_3Cl_5CH_2SiMe_3}$ (**1a**)	$\mathrm{P}\mathit{CH_2}\mathrm{SiMe_3}$	1.84 (dt, 2 H)	29.20 (dt)	$J_{\mathrm{PCH}} = 23.4$	
	$\mathrm{PCH_2Si}\mathit{Me_3}$	0.26 (s, 9 H)	−0.43 (d)	$J_{\mathrm{PNPCH}} = 4.7$	
				$J_{\mathrm{PC}} = 110.9$	
				$J_{\mathrm{PNPC}} = 8.0$	
				$J_{\mathrm{PCSiC}} = 4.4$	
$\mathrm{N_3P_3Cl_5CH_2SiMe_2OSiMe_3}$ (**1b**)	$\mathrm{P}\mathit{CH_2}\mathrm{SiMe_2OSiMe_3}$	1.87 (dt, 2 H)	30.97 (dt)	$J_{\mathrm{PCH}} = 23.8$	
	$\mathrm{PCH_2Si}\mathit{Me_2}\mathrm{OSiMe_3}$	0.30 (s, 6 H)	1.84 (s)	$J_{\mathrm{PNPCH}} = 4.4$	
	$\mathrm{PCH_2SiMe_2OSi}\mathit{Me_3}$	0.08 (s, 9 H)	1.89 (s)	$J_{\mathrm{PC}} = 111.4$	
				$J_{\mathrm{PNPC}} = 8.0$	
$\mathrm{N_3P_3Cl_5CH_2\overline{Si(Me)(OSiMe_2)_3O}}$ (**1c**)	$\mathrm{P}\mathit{CH_2}\mathrm{Si}$	1.92 (dt, 2 H)	30.32 (dt)	$J_{\mathrm{PCH}} = 23.7$	
	$\mathrm{PCH_2Si}\mathit{Me}$	0.38 (s, 3 H)	0.87 (s)	$J_{\mathrm{PNPCH}} = 4.1$	
	$\mathrm{(OSi}\mathit{Me_2}\mathrm{)(OSiMe_2)(OSi}\mathit{Me_2}\mathrm{)}$	0.16 (s, 6 H)	0.75 (s)	$J_{\mathrm{PC}} = 114.1$	
		0.13 (s, 6 H)		$J_{\mathrm{PNPC}} = 7.8$	
	$\mathrm{(OSiMe_2)(OSi}\mathit{Me_2}\mathrm{)(OSiMe_2)}$	0.12 (s, 3 H)	0.72 (s)		
		0.11 (s, 3 H)			
gem-$\mathrm{N_3P_3Cl_4(CH_2SiMe_3)_2}$ (**2a**)	$\mathrm{P}\mathit{CH_2}\mathrm{SiMe_3}$	1.32 (dt, 4 H)	25.81 (dt)	$J_{\mathrm{PCH}} = 17.7$	
	$\mathrm{PCH_2Si}\mathit{Me_3}$	0.22 (s, 18 H)	0.01 (d)	$J_{\mathrm{PNPCH}} = 2.9$	
				$J_{\mathrm{PC}} = 82.4$	
				$J_{\mathrm{PNPC}} = 3.8$	
				$J_{\mathrm{PCSiC}} = 3.1$	
gem-$\mathrm{N_3P_3Cl_4(CH_2SiMe_2OSiMe_3)_2}$ (**2b**)	$\mathrm{P}\mathit{CH_2}\mathrm{SiMe_2OSiMe_3}$	1.41 (dt, 4 H)	27.10 (dt)	$J_{\mathrm{PCH}} = 18.8$	
	$\mathrm{PCH_2Si}\mathit{Me_2}\mathrm{OSiMe_3}$	0.27 (s, 12 H)	2.20 (d)	$J_{\mathrm{PNPCH}} = 2.6$	
	$\mathrm{PCH_2SiMe_2OSi}\mathit{Me_3}$	0.08 (s, 18 H)	1.92 (s)	$J_{\mathrm{PC}} = 81.6$	
				$J_{\mathrm{PNPC}} = 3.8$	
				$J_{\mathrm{PCSiC}} = 1.1$	
gem-$\mathrm{N_3P_3Cl_4[CH_2\overline{Si(Me)(OSiMe_2)_3O}]_2}$ (**2c**)	$\mathrm{P}\mathit{CH_2}\mathrm{Si}$	1.50 (dt, 4 H)	26.08 (dt)	$J_{\mathrm{PCH}} = 19.2$	
	$\mathrm{PCH_2Si}\mathit{Me}$	0.36 (s, 6 H)	1.27 (s)	$J_{\mathrm{PNPCH}} = 2.4$	
	$\mathrm{(OSi}\mathit{Me_2}\mathrm{)(OSiMe_2)(OSi}\mathit{Me_2}\mathrm{)}$	0.14 (s, 12 H)	0.81 (s)	$J_{\mathrm{PC}} = 83.2$	
		0.13 (s, 12 H)	0.77 (s)	$J_{\mathrm{PNPC}} = 3.5$	
	$\mathrm{(OSiMe_2)(OSi}\mathit{Me_2}\mathrm{)(OSiMe_2)}$	0.11 (s, 12 H)	0.71 (s)		
				$\mathrm{PCH_3}$	$\mathrm{PCH_2Si}$
gem-$\mathrm{N_3P_3Cl_4(Me)(CH_2SiMe_3)}$ (**3a**)	$\mathrm{P}\mathit{CH_3}$	1.69 (d, 3 H)	23.33 (dt)	$J_{\mathrm{PCH}} = 14.1$	$J_{\mathrm{PCH}} = 17.2$
	$\mathrm{P}\mathit{CH_2}\mathrm{SiMe_3}$	1.31 (dt, 2 H)	23.16 (dt)	J_{PNPCH} = unresolved	$J_{\mathrm{PNPCH}} = 3.9$
	$\mathrm{PCH_2Si}\mathit{Me_3}$	0.23 (s, 9 H)	−0.15 (d)	$J_{\mathrm{PC}} = 88.9$	$J_{\mathrm{PC}} = 88.6$
				$J_{\mathrm{PNPC}} = 2.5$	$J_{\mathrm{PNPC}} = 5.1$
					$J_{\mathrm{PCSiC}} = 3.4$
gem-$\mathrm{N_3P_3Cl_4(Me)(CH_2SiMe_2OSiMe_3)}$ (**3b**)	$\mathrm{P}\mathit{CH_3}$	1.69 (dt, 3 H)	25.53 (dt)	$J_{\mathrm{PCH}} = 14.3$	$J_{\mathrm{PCH}} = 18.7$
	$\mathrm{P}\mathit{CH_2}\mathrm{SiMe_2OSiMe_3}$	1.38 (dt, 2 H)	22.55 (dt)	$J_{\mathrm{PNPCH}} = 1.6$	$J_{\mathrm{PNPCH}} = 2.9$
	$\mathrm{PCH_2Si}\mathit{Me_2}\mathrm{OSiMe_3}$	0.29 (s, 6 H)	2.12 (d)	$J_{\mathrm{PC}} = 83.2$	$J_{\mathrm{PC}} = 93.1$
	$\mathrm{PCH_2SiMe_2OSi}\mathit{Me_3}$	0.10 (s, 9 H)	1.89 (s)	$J_{\mathrm{PNPC}} = 4.8$	$J_{\mathrm{PNPC}} = 2.6$
					$J_{\mathrm{PCSiC}} = 2.3$
gem-$\mathrm{N_3P_3Cl_4(Me)[CH_2\overline{Si(Me)(OSiMe_2)_3O}]}$ (**3c**)	$\mathrm{P}\mathit{CH_3}$	1.69 (dt, 3 H)	25.34 (dt)	$J_{\mathrm{PCH}} = 14.6$	$J_{\mathrm{PCH}} = 19.6$
	$\mathrm{P}\mathit{CH_2}\mathrm{Si}$	1.41 (dt, 2 H)	21.91 (dt)	$J_{\mathrm{PNPCH}} = 1.8$	J_{PNPCH} = unresolved
	$\mathrm{PCH_2Si}\mathit{Me}$	0.34 (s, 3 H)	1.14 (s)	$J_{\mathrm{PC}} = 82.1$	$J_{\mathrm{PC}} = 94.9$
	$\mathrm{(OSi}\mathit{Me_2}\mathrm{)(OSiMe_2)OSi}\mathit{Me_2}\mathrm{)}$	0.13 (s, 12 H)	0.80 (s)	$J_{\mathrm{PNPC}} = 4.0$	$J_{\mathrm{PNPC}} = 3.0$
	$\mathrm{(OSiMe_2)(OSi}\mathit{Me_2}\mathrm{)(OSiMe_2)}$	0.10 (s, 6 H)	0.80 (s)		
$\mathrm{N_3P_3(OCH_2CF_3)_5CH_2SiMe_3}$ (**9a**)	$\mathrm{P}\mathit{CH_2}\mathrm{SiMe_3}$	1.30 (dt, 2 H)	20.22 (dt)	$J_{\mathrm{PCH}} = 22.3$	
	$\mathrm{PCH_2Si}\mathit{Me_3}$	0.17 (s, 9 H)	−0.57 (d)	$J_{\mathrm{PNPCH}} = 1.8$	
	$\mathrm{P(O}\mathit{CH_2}\mathrm{CF_3)_2}$	4.24 (m, 8 H)	62.72 (qm)	$J_{\mathrm{PC}} = 131.8$	
	$\mathrm{P(O}\mathit{CH_2}\mathrm{CF_3)(C)}$	4.06 (p, 2 H)	60.26 (qd)	$J_{\mathrm{PNPC}} = 6.1$	
	$\mathrm{POCH_2}\mathit{CF_3}$	...	122.60 (qt)	$J_{\mathrm{PCSiC}} = 3.7$	
$\mathrm{N_3P_3(OCH_2CF_3)_5CH_2SiMe_2OSiMe_3}$ (**9b**)	$\mathrm{P}\mathit{CH_2}\mathrm{SiMe_2OSiMe_3}$	1.40 (dt, 2 H)	22.39 (dt)	$J_{\mathrm{PCH}} = 22.5$	

	$\mathrm{PCH_2Si\mathit{Me}_2OSiMe_3}$	0.25 (s, 6 H)	1.65 (s)	J_{PNPCH} = 1.6	
	$\mathrm{PCH_2SiMe_2OSi\mathit{Me}_3}$	0.08 (s, 9 H)	1.65 (s)	J_{PC} = 131.8	
	$\mathrm{P(O\mathit{CH}_2CF_3)_2}$	4.25 (m, 8 H)	62.78 (qd)	J_{PNPC} = 6.1	
	$\mathrm{P(O\mathit{CH}_5CF_3)(C)}$	4.07 (p, 2 H)	60.38 (qd)		
	$\mathrm{POCH_2\mathit{C}F_3}$	...	122.64 (qt)		
$\mathrm{N_3P_3(OCH_2CF_3)_5[CH_2\overline{Si(Me)(OSiMe_2)_3O}]}$ (**9c**)	$\mathrm{P\mathit{CH}_2Si}$	1.43 (dt, 2 H)	21.82 (dt)	J_{PCH} = 22.7	
	$\mathrm{PCH_2Si\mathit{Me}}$	0.30 (s, 3 H)	0.51 (s)	J_{PNPCH} = unresolved	
	$\mathrm{(OSi\mathit{Me}_2)(OSiMe_2)(OSi\mathit{Me}_2)}$	0.121 (s, 6 H)	0.51 (s)	J_{PC} = 133.1	
		0.117 (s, 6 H)		J_{PNPC} = 6.1	
	$\mathrm{(OSiMe_2)(OSi\mathit{Me}_2)(OSiMe_2)}$	0.107 (s, 6 H)	0.51 (s)		
	$\mathrm{P(O\mathit{CH}_2CF_3)_2}$	4.26 (m, 8 H)	62.78 (q)		
	$\mathrm{P(O\mathit{CH}_2CF_3)(C)}$	4.10 (p, 2 H)	60.72 (q)		
	$\mathrm{POCH_2\mathit{C}F_3}$	...	122.61 (q)		
gem-$\mathrm{N_3P_3(OCH_2CF_3)_4(CH_2SiMe_3)_2}$ (**11a**)	$\mathrm{P\mathit{CH}_2SiMe_3}$	1.22 (dt, 4 H)	26.37 (dt)	J_{PCH} = 17.9	
	$\mathrm{PCH_2Si\mathit{Me}_3}$	0.16 (s, 18 H)	−0.14 (d)	J_{PNPCH} = 2.0	
	$\mathrm{PO\mathit{CH}_2CF_3}$	4.22 (m, 8 H)	62.45 (q)	J_{PC} = 84.2	
	$\mathrm{POCH_2\mathit{C}F_3}$	...	122.80 (qt)	J_{PNPC} = 3.7	
				J_{PCSiC} = 2.4	
gem-$\mathrm{N_3P_3(OCH_2CF_3)_4(CH_2SiMe_2OSiMe_3)_2}$ (**11b**)	$\mathrm{P\mathit{CH}_2SiMe_2OSiMe_3}$	1.34 (dt, 4 H)	27.84 (d)	J_{PCH} = 18.9	
	$\mathrm{PCH_2Si\mathit{Me}_2OSiMe_3}$	0.24 (s, 12 H)	2.13 (s)	J_{PNPCH} = unresolved	
	$\mathrm{PCH_2SiMe_2OSi\mathit{Me}_3}$	0.10 (s, 18 H)	1.92 (s)	J_{PC} = 84.2	
	$\mathrm{PO\mathit{CH}_2CF_3}$	4.22 (m, 8 H)	62.48 (q)	J_{PNPC} = unresolved	
	$\mathrm{POCH_2\mathit{C}F_3}$	...	122.83 (qt)		
gem-$\mathrm{N_3P_3(OCH_2CF_3)_4[CH_2\overline{Si(Me)(OSiMe_2)_3O}]_2}$ (**11c**)	$\mathrm{P\mathit{CH}_2Si}$	1.41 (dt, 4 H)	26.73 (d)	J_{PCH} = 19.4	
	$\mathrm{PCH_2Si\mathit{Me}}$	0.30 (s, 6 H)	1.16 (s)	J_{PNPCH} = unresolved	
	$\mathrm{(OSi\mathit{Me}_2)(OSiMe_2)(OSi\mathit{Me}_2)}$	0.13 (s, 12 H)	0.67 (s)	J_{PC} = 85.5	
		0.12 (s, 12 H)		J_{PNPC} = unresolved	
	$\mathrm{(OSiMe_2)(OSi\mathit{Me}_2)(OSiMe_2)}$	0.11 (s, 12 H)	0.67 (s)		
	$\mathrm{PO\mathit{CH}_2CF_3}$	4.24 (m, 8 H)	62.45 (q)		
	$\mathrm{POCH_2\mathit{C}F_3}$	...	122.83 (qt)		
				$\mathrm{PCH_3}$	$\mathrm{PCH_2Si}$
gem-$\mathrm{N_3P_3(OCH_2CF_3)(Me)(CH_2SiMe_3)}$ (**13a**)	$\mathrm{P\mathit{CH}_3}$	1.52 (dt, 3 H)	24.22 (dt)	J_{PCH} = 13.9	J_{PCH} = 18.3
	$\mathrm{P\mathit{CH}_2SiMe_3}$	1.22 (dt, 2 H)	23.59 (dt)	J_{PNPCH} = unresolved	J_{PNPCH} = unresolved
	$\mathrm{PCH_2Si\mathit{Me}_3}$	0.16 (s, 9 H)	−0.19 (d)	J_{PC} = 86.3	J_{PC} = 94.0
	$\mathrm{PO\mathit{CH}_2CF_3}$	4.20 (m, 8 H)	62.59 (qd)	J_{PNPC} = 4.3	J_{PNPC} = 2.6
	$\mathrm{POCH_2\mathit{C}F_3}$	...	122.76 (qt)		J_{PCSiC} = 3.4
gem-$\mathrm{N_3P_3(OCH_2CF_3)_4(Me)(CH_2SiMe_2OSiMe_3)}$ (**13b**)	$\mathrm{P\mathit{CH}_3}$	1.56 (dt, 3 H)	26.56 (dt)	J_{PCH} = 14.2	J_{PCH} = 19.5
	$\mathrm{P\mathit{CH}_2SiMe_2OSiMe_3}$	1.28 (dt, 2 H)	22.88 (dt)	J_{PNPCH} = unresolved	J_{PNPCH} = unresolved
	$\mathrm{PCH_2Si\mathit{Me}_2OSiMe_3}$	0.23 (s, 6 H)	2.00 (d)	J_{PC} = 83.0	J_{PC} = 95.2
	$\mathrm{PCH_2SiMe_2OSi\mathit{Me}_3}$	0.08 (s, 9 H)	1.76 (s)	J_{PNPC} = 4.0	J_{PNPC} = 3.1
	$\mathrm{PO\mathit{CH}_2CF_3}$	4.22 (m, 8 H)	62.51 (qd)		J_{PCSiC} = 2.4
	$\mathrm{POCH_2\mathit{C}F_3}$	...	122.80 (qt)		
gem-$\mathrm{N_3P_3(OCH_2CF_3)_4(Me)[CH_2\overline{Si(Me)(OSiMe_2)_3O}]}$ (**13c**)	$\mathrm{P\mathit{CH}_3}$	1.59 (dt, 3 H)	26.10 (dt)	J_{PCH} = 14.4	J_{PCH} = 20.2
	$\mathrm{P\mathit{CH}_2SiMe}$	1.31 (dt, 2 H)	22.18 (dt)	J_{PNPCH} = unresolved	J_{PNPCH} = unresolved
	$\mathrm{PCH_2Si\mathit{Me}}$	0.30 (s, 3 H)	2.19 (s)	J_{PC} = 81.8	J_{PC} = 95.2
	$\mathrm{(OSi\mathit{Me}_2)(OSiMe_2)(OSi\mathit{Me}_2)}$	0.12 (s, 12 H)	0.51 (s)	J_{PNPC} = unresolved	J_{PNPC} = unresolved
	$\mathrm{(OSiMe_2)(OSi\mathit{Me}_2)(OSiMe_2)}$	0.11 (s, 6 H)	0.89 (s)		
	$\mathrm{PO\mathit{CH}_2CF_3}$	4.24 (m, 8 H)	62.54 (q)		
	$\mathrm{POCH_2\mathit{C}F_3}$	...	122.78 (qt)		
gem-$\mathrm{N_3P_3(OCH_2CF_3)_4(CH_3)_2}$ (**12**)	$\mathrm{P\mathit{CH}_3}$	1.57 (dt, 6 H)	21.32 (dt)	J_{PCH} = 14.6	
	$\mathrm{PO\mathit{CH}_2CF_3}$	4.24 (m, 8 H)	62.59 (qt)	J_{PNPCH} = 1.7	
	$\mathrm{POCH_2\mathit{C}F_3}$	...	122.69 (qt)	J_{PC} = 96.1	
				J_{PNPC} = 3.4	

[a] All spectra were obtained with $\mathrm{CDCl_3}$ as a solvent. [b] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet.

Table IV. Bond Lengths (Å) for *gem*-$N_3P_3Cl_4[CH_2Si(Me)(OSiMe_2)_3O]_2$ (2c)

Cl(1)–P(2)	1.993 (3)	Si(3)–C(5)	1.841 (7)
Cl(2)–P(2)	2.000 (3)	Si(3)–C(6)	1.822 (7)
Cl(3)–P(3)	1.996 (3)	Si(4)–O(3)	1.624 (4)
Cl(4)–P(3)	1.999 (3)	Si(4)–O(4)	1.625 (4)
P(1)–N(1)	1.621 (5)	Si(4)–C(7)	1.880 (7)
P(1)–N(3)	1.625 (4)	Si(4)–C(8)	1.863 (7)
P(1)–C(1)	1.802 (5)	Si(5)–O(5)	1.601 (5)
P(1)–C(9)	1.789 (5)	Si(5)–O(8)	1.619 (5)
P(2)–N(1)	1.550 (4)	Si(5)–C(9)	1.883 (5)
P(2)–N(2)	1.581 (5)	Si(5)–C(10)	1.890 (6)
P(3)–N(2)	1.539 (5)	Si(6)–O(5)	1.630 (5)
P(3)–N(3)	1.552 (4)	Si(6)–O(6)	1.597 (6)
Si(1)–O(1)	1.610 (4)	Si(6)–C(11)	1.871 (8)
Si(1)–O(4)	1.609 (4)	Si(6)–C(12)	1.843 (8)
Si(1)–C(1)	1.902 (5)	Si(7)–O(6)	1.547 (6)
Si(1)–C(2)	1.845 (6)	Si(7)–O(7)	1.610 (5)
Si(2)–O(1)	1.625 (4)	Si(7)–C(13)	1.730 (11)
Si(2)–O(2)	1.604 (4)	Si(7)–C(14)	1.75 (2)
Si(2)–C(3)	1.926 (7)	Si(8)–O(7)	1.605 (5)
Si(2)–C(4)	1.860 (7)	Si(8)–O(8)	1.615 (4)
Si(3)–O(2)	1.597 (4)	Si(8)–C(15)	1.856 (9)
Si(3)–O(3)	1.616 (4)	Si(8)–C(16)	1.881 (9)

Table V. Bond Lengths (Å) for *gem*-$N_3P_3Cl_4(Me)[CH_2Si(Me)(OSiMe_2)_3O]$ (3c)

Cl(1)–P(2)	1.995 (2)	Si(1)–C(2)	1.864 (4)
Cl(2)–P(2)	2.004 (2)	Si(1)–C(3)	1.851 (5)
Cl(3)–P(3)	2.002 (2)	Si(2)–O(1)	1.609 (3)
Cl(4)–P(3)	1.996 (2)	Si(2)–O(2)	1.599 (4)
P(1)–N(1)	1.627 (3)	Si(2)–C(4)	1.839 (7)
P(1)–N(3)	1.623 (4)	Si(2)–C(5)	1.870 (8)
P(1)–C(1)	1.808 (4)	Si(3)–O(2)	1.599 (4)
P(1)–C(2)	1.781 (4)	Si(3)–O(3)	1.617 (4)
P(2)–N(1)	1.557 (3)	Si(3)–C(6)	1.864 (9)
P(2)–N(2)	1.587 (3)	Si(3)–C(7)	1.818 (8)
P(3)–N(2)	1.558 (3)	Si(4)–O(3)	1.606 (4)
P(3)–N(3)	1.554 (4)	Si(4)–O(4)	1.633 (3)
Si(1)–O(1)	1.614 (3)	Si(4)–C(8)	1.843 (8)
Si(1)–O(4)	1.611 (3)	Si(4)–C(9)	1.867 (9)

Table VI. Bond Angles (deg) for *gem*-$N_3P_3Cl_4[CH_2Si(Me)(OSiMe_2)_3O]_2$ (2c)

N(1)–P(1)–N(3)	113.7 (2)	O(4)–Si(4)–C(8)	107.4 (3)
N(1)–P(1)–C(1)	109.8 (3)	C(7)–Si(4)–C(8)	113.9 (4)
N(1)–P(1)–C(9)	110.5 (3)	O(5)–Si(5)–O(8)	110.4 (2)
N(3)–P(1)–C(1)	107.8 (2)	O(5)–Si(5)–C(9)	111.1 (3)
N(3)–P(1)–C(9)	108.5 (2)	O(5)–Si(5)–C(10)	108.8 (3)
C(1)–P(1)–C(9)	106.3 (3)	O(8)–Si(5)–C(9)	102.9 (3)
Cl(1)–P(2)–Cl(2)	99.8 (2)	O(8)–Si(5)–C(10)	110.5 (3)
Cl(1)–P(2)–N(1)	109.7 (2)	C(9)–Si(5)–C(10)	113.1 (3)
Cl(1)–P(2)–N(2)	108.3 (3)	O(5)–Si(6)–O(6)	108.3 (3)
Cl(2)–P(2)–N(1)	110.3 (2)	O(5)–Si(6)–C(11)	108.5 (3)
Cl(2)–P(2)–N(2)	107.6 (3)	O(5)–Si(6)–C(12)	109.2 (4)
N(1)–P(2)–N(2)	119.4 (3)	O(6)–Si(6)–C(11)	109.3 (4)
Cl(3)–P(3)–Cl(4)	100.1 (1)	O(6)–Si(6)–C(12)	109.0 (4)
Cl(3)–P(3)–N(2)	107.1 (3)	C(11)–Si(6)–C(12)	112.4 (5)
Cl(3)–P(3)–N(3)	110.2 (2)	O(6)–Si(7)–O(7)	111.2 (3)
Cl(4)–P(3)–N(2)	108.9 (3)	O(6)–Si(7)–C(13)	115.1 (7)
Cl(4)–P(3)–N(3)	107.8 (2)	O(6)–Si(7)–C(14)	112.2 (7)
N(2)–P(3)–N(3)	120.8 (3)	O(7)–Si(7)–C(13)	108.9 (5)
O(1)–Si(1)–O(4)	109.5 (2)	O(7)–Si(7)–C(14)	108.6 (7)
O(1)–Si(1)–C(1)	104.9 (2)	C(13)–Si(7)–C(14)	100.1 (1)
O(1)–Si(1)–C(2)	111.0 (3)	O(7)–Si(8)–O(8)	109.1 (3)
O(4)–Si(1)–C(1)	108.4 (2)	O(7)–Si(8)–C(15)	112.2 (5)
O(4)–Si(1)–C(2)	109.7 (3)	O(7)–Si(8)–C(16)	106.2 (4)
C(1)–Si(1)–C(2)	113.3 (3)	O(8)–Si(8)–C(15)	110.0 (4)
O(1)–Si(2)–O(2)	108.8 (2)	O(8)–Si(8)–C(16)	108.3 (3)
O(1)–Si(2)–C(3)	110.6 (3)	C(15)–Si(8)–C(16)	110.8 (6)
O(1)–Si(2)–C(4)	107.7 (3)	Si(1)–O(1)–Si(2)	149.4 (3)
O(2)–Si(2)–C(3)	106.1 (3)	Si(2)–O(2)–Si(3)	156.8 (3)
O(2)–Si(2)–C(4)	110.9 (3)	Si(3)–O(3)–Si(4)	145.3 (3)
C(3)–Si(2)–C(4)	112.8 (4)	Si(1)–O(4)–Si(4)	148.3 (3)
O(2)–Si(3)–O(3)	109.5 (2)	Si(5)–O(5)–Si(6)	153.0 (3)
O(2)–Si(3)–C(5)	110.0 (3)	Si(6)–O(6)–Si(7)	160.9 (4)
O(2)–Si(3)–C(6)	108.8 (3)	Si(7)–O(7)–Si(8)	146.8 (4)
O(3)–Si(3)–C(5)	108.5 (3)	Si(5)–O(8)–Si(8)	153.4 (3)
O(3)–Si(3)–C(6)	109.4 (3)	P(1)–N(1)–P(2)	122.7 (3)
C(5)–Si(3)–C(6)	110.6 (4)	P(2)–N(2)–P(3)	119.8 (3)
O(3)–Si(4)–O(4)	109.4 (2)	P(1)–N(3)–P(3)	121.3 (3)
O(3)–Si(4)–C(7)	107.7 (3)	P(1)–C(1)–Si(1)	118.5 (3)
O(3)–Si(4)–C(8)	109.8 (3)	P(1)–C(9)–Si(5)	120.1 (3)
O(4)–Si(4)–C(7)	108.6 (3)		

in THF, 0.13 mol) was added dropwise over a 40-min period. The reaction mixture was then stirred at 25 °C for 16 h. The solvent was removed under reduced pressure, and diethyl ether (250 mL) was added to the residue. The residue was washed with 3–250-mL portions of a 5% aqueous HCl solution, and the ether layer was dried over $MgSO_4$. Suction filtration through Fuller's Earth yielded a clear solution from which the ether was removed under reduced pressure to yield the crude product. In each case the product was recrystallized from hexane or dry ice/2-propanol-chilled pentane to yield a white solid, which sublimed at 60–100 °C (0.05 mmHg). See Tables I–III for complete characterization data. **Method b.** Hexachlorocyclotriphosphazene (5.00 g, 0.0144 mol) and $[(n\text{-}Bu)_3PCuI]_4$ (4.00 g, 0.00250 mol) were stirred together in dry THF (150 mL) at −78 °C under an atmosphere of dry nitrogen. Methylmagnesium chloride (26 mL of a 2.9 M solution in THF, 0.075 mol) was added dropwise over a period of 30 min. The reaction mixture was then stirred for 16 h as the temperature was allowed to rise to 25 °C. The reaction mixture was then cooled to 0 °C, and (iodomethyl)trimethylsilane, (iodomethyl)pentamethyldisiloxane, or (iodomethyl)heptamethylcyclotetrasiloxane (0.081 mol) was added dropwise over a 30-min period. The reaction mixture was then refluxed at 66 °C for 18 h. The product 3 was isolated and purified, as described above in method a.

Synthesis of $N_3P_3(OCH_2CF_3)_5R$ [R = $-CH_2SiMe_3$ (9a) and R = $-CH_2SiMe_2OSiMe_3$ (9b)]. Trifluoroethanol (4.13 g, 0.0413 mol) was dissolved in dry toluene (20 mL) and was added slowly to a slurry of NaH (0.90 g, 0.038 mol) in dry toluene (150 mL). After being stirred at 25 °C for 2 h, followed by gentle heating for 3 h and refluxing at 110 °C for 1 h, the CF_3CH_2ONa slurry was cooled to 25 °C. $N_3P_3Cl_5R$, R = $-CH_2SiMe_3$ (**1a**) or R = $-CH_2SiMe_2OSiMe_3$ (**1b**) (0.00500 mol), was then added to the reaction mixture, which was refluxed at 110 °C for 1 h. On cooling, the reaction mixture was poured into 5% HCl (250 mL) and then extracted with 3–100-mL portions of diethyl ether. The ethereal layer was dried over $MgSO_4$ and filtered through Fuller's Earth, and the ether was removed under reduced pressure to yield an oil. The oil was purified further by column chromatography or preparative liquid chromatography on silica gel, followed by vacuum distillation (90–130 °C (0.05 mmHg)). See Tables I–III for complete characterization data.

Synthesis of *gem*-$N_3P_3(OCH_2CF_3)_4R_2$ [R = $-CH_2SiMe_3$ (11a) and R = $-CH_2SiMe_2OSiMe_3$ (11b)] and *gem*-$N_3P_3(OCH_2CF_3)_4(Me)R$ [R = $-CH_2SiMe_3$ (13a) and R = $-CH_2SiMe_2OSiMe_3$ (13b)]. Sodium trifluoroethoxide was prepared in toluene, as described above, using CF_3CH_2OH (3.30 g, 0.0330 mol) and NaH (0.72 g, 0.0300 mol). To the slurry of CF_3CH_2ONa in toluene was added *gem*-$N_3P_3Cl_4R_2$ [R = $-CH_2SiMe_3$ (**2a**) or R = $-CH_2SiMe_2OSiMe_3$ (**2b**)] (0.00500 mol) or *gem*-$N_3P_3Cl_4(Me)R$ [R = $-CH_2SiMe_3$ (**3a**) or R = $-CH_2SiMe_2OSiMe_3$ (**3b**)] (0.00500 mol). The reaction mixture was then refluxed at 110 °C for 24 h (**11a** and **11b**) or 72 h (**13a** and **13b**). The products were isolated and purified as described above. See Tables I–III for complete characterization data.

Synthesis of $N_3P_3(OCH_2CF_3)_5R$ (9c), *gem*-$N_3P_3(OCH_2CF_3)_4R_2$ (11c), and *gem*-$N_3P_3(OCH_2CF_3)_4(Me)R$ (13c) [R = $-CH_2Si(Me)(OSiMe_2)_3O$]. Sodium trifluoroethoxide was prepared in dioxane by the careful addition of CF_3CH_2OH (4.13 g, 0.0413 mol, for **9c**; 3.30 g, 0.0330 mol, for **11c** and **13c**) in dry dioxane (20 mL) to a slurry of NaH (0.90 g, 0.0375 mol, for **9c**; 0.72 g, 0.0300 mol, for **11c** and **13c**) in dry dioxane (100 mL). On completion of hydrogen evolution, $N_3P_3Cl_5R$ (**1c**), *gem*-$N_3P_3Cl_4R_2$ (**2c**), or *gem*-$N_3P_3Cl_4(Me)R$ (**3c**) [R = $-CH_2Si(Me)(OSiMe_2)_3O$] (0.00500 mol) was added to the appropriate CF_3CH_2ONa solution. The solution was stirred at 25 °C for 0.75 (**9c**), 18 (**11c**), or 2.0 h (**13c**) and then immediately poured into 5% HCl (250 mL). The

Table VII. Bond Angles (deg) for *gem*-$N_3P_3Cl_4(Me)[CH_2Si(Me)(OSiMe_2)_3O]$ (3c)

N(1)–P(1)–N(3)	114.0 (2)	O(1)–Si(2)–C(4)	109.4 (3)
N(1)–P(1)–C(1)	108.0 (2)	O(1)–Si(2)–C(5)	106.7 (3)
N(1)–P(1)–C(2)	109.1 (2)	O(2)–Si(2)–C(4)	108.5 (3)
N(3)–P(1)–C(1)	109.8 (2)	O(2)–Si(2)–C(5)	110.6 (3)
N(3)–P(1)–C(2)	110.0 (2)	C(4)–Si(2)–C(5)	113.2 (3)
C(1)–P(1)–C(2)	105.5 (2)	O(2)–Si(3)–O(3)	109.3 (2)
Cl(1)–P(2)–Cl(2)	100.03 (9)	O(2)–Si(3)–C(6)	108.8 (4)
Cl(1)–P(2)–N(1)	108.6 (2)	O(2)–Si(3)–C(7)	108.9 (4)
Cl(1)–P(2)–N(2)	108.5 (1)	O(3)–Si(3)–C(6)	108.6 (4)
Cl(2)–P(2)–N(1)	109.7 (2)	O(3)–Si(3)–C(7)	110.5 (3)
Cl(2)–P(2)–N(2)	108.3 (2)	C(6)–Si(3)–C(7)	110.6 (5)
N(1)–P(2)–N(2)	119.8 (2)	O(3)–Si(4)–O(4)	108.7 (2)
Cl(3)–P(3)–Cl(4)	100.07 (8)	O(3)–Si(4)–C(8)	108.3 (3)
Cl(3)–P(3)–N(2)	107.8 (2)	O(3)–Si(4)–C(9)	109.1 (3)
Cl(3)–P(3)–N(3)	110.4 (2)	O(4)–Si(4)–C(8)	109.0 (3)
Cl(4)–P(3)–N(2)	108.0 (2)	O(4)–Si(4)–C(9)	109.4 (3)
Cl(4)–P(3)–N(3)	108.5 (2)	C(8)–Si(4)–C(9)	112.3 (4)
N(2)–P(3)–N(3)	120.2 (2)	Si(1)–O(1)–Si(2)	151.8 (3)
O(1)–Si(1)–O(4)	108.6 (2)	Si(2)–O(2)–Si(3)	154.9 (3)
O(1)–Si(1)–C(2)	103.5 (2)	Si(3)–O(3)–Si(4)	153.4 (3)
O(1)–Si(1)–C(3)	111.3 (3)	Si(1)–O(4)–Si(4)	139.9 (2)
O(4)–Si(1)–C(2)	111.1 (2)	P(1)–N(1)–P(2)	121.7 (2)
O(4)–Si(1)–C(3)	109.7 (3)	P(2)–N(2)–P(3)	119.7 (2)
C(2)–Si(1)–C(3)	112.5 (2)	P(1)–N(3)–P(3)	122.6 (2)
O(1)–Si(2)–O(2)	108.5 (2)	P(1)–C(2)–Si(1)	121.2 (2)

Table VIII. Positional Parameters and Their Estimated Standard Deviations for *gem*-$N_3P_3Cl_4[CH_2Si(Me)(OSiMe_2)_3O]_2$ (2c)

atom	*x*	*y*	*z*
Cl(1)	0.3759 (5)	0.3008 (3)	0.4296 (3)
Cl(2)	0.5163 (4)	0.1458 (4)	0.4490 (3)
Cl(3)	0.1790 (4)	−0.1230 (3)	0.2724 (3)
Cl(4)	0.0072 (4)	0.0013 (4)	0.2243 (2)
P(1)	0.1760 (3)	0.1261 (2)	0.5396 (2)
P(2)	0.3430 (3)	0.1737 (2)	0.4388 (2)
P(3)	0.1462 (3)	0.0184 (3)	0.3320 (2)
Si(1)	0.3325 (3)	0.1283 (2)	0.7307 (2)
Si(2)	0.4016 (3)	0.0165 (2)	0.8518 (2)
Si(3)	0.2834 (3)	0.1628 (2)	1.0276 (2)
Si(4)	0.2514 (3)	0.2898 (2)	0.9191 (2)
Si(5)	0.0201 (3)	0.3020 (2)	0.5842 (2)
Si(6)	0.2400 (4)	0.4914 (3)	0.6820 (3)
Si(7)	0.0784 (5)	0.6177 (3)	0.8281 (3)
Si(8)	−0.1408 (4)	0.4345 (3)	0.7328 (3)
O(1)	0.3449 (7)	0.0449 (5)	0.7668 (4)
O(2)	0.3638 (7)	0.0894 (5)	0.9560 (5)
O(3)	0.2241 (7)	0.2247 (5)	0.9764 (5)
O(4)	0.2639 (7)	0.2135 (5)	0.8047 (4)
O(5)	0.1338 (7)	0.3903 (5)	0.6068 (5)
O(6)	0.1779 (9)	0.5687 (7)	0.7681 (7)
O(7)	−0.0367 (9)	0.5324 (6)	0.8119 (6)
O(8)	−0.0728 (7)	0.3463 (5)	0.6616 (6)
N(1)	0.2963 (7)	0.1964 (6)	0.5371 (5)
N(2)	0.2624 (9)	0.0867 (7)	0.3344 (6)
N(3)	0.0933 (7)	0.0450 (6)	0.4286 (5)
C(1)	0.2262 (9)	0.0558 (7)	0.6009 (6)
C(2)	0.4871 (11)	0.1889 (9)	0.7304 (8)
C(3)	0.5814 (11)	0.0436 (9)	0.8774 (8)
C(4)	0.3340 (15)	−0.1190 (8)	0.8072 (11)
C(5)	0.1552 (13)	0.0866 (10)	1.0448 (9)
C(6)	0.3899 (16)	0.2562 (11)	1.1524 (9)
C(7)	0.1143 (13)	0.3518 (9)	0.9138 (9)
C(8)	0.4033 (15)	0.3812 (10)	0.9842 (9)
C(9)	0.0765 (9)	0.2035 (7)	0.6127 (6)
C(10)	−0.0669 (14)	0.2472 (9)	0.4498 (8)
C(11)	0.3688 (15)	0.4515 (11)	0.7409 (11)
C(12)	0.2945 (19)	0.5529 (10)	0.6119 (11)
C(13)	0.1333 (24)	0.6981 (20)	0.9546 (15)
C(14)	0.0195 (25)	0.6996 (16)	0.7900 (23)
C(15)	−0.2560 (18)	0.4632 (15)	0.6553 (14)
C(16)	−0.2216 (16)	0.3879 (11)	0.8086 (11)

Table IX. Positional Parameters and Their Estimated Standard Deviations for *gem*-$N_3P_3Cl_4(Me)[CH_2Si(Me)(OSiMe_2)_3O]$ (3c)

atom	*x*	*y*	*z*
Cl(1)	0.3527 (1)	0.5038 (2)	0.3832 (1)
Cl(2)	0.5480 (2)	0.6006 (3)	0.4396 (1)
Cl(3)	0.4780 (2)	1.1359 (2)	0.4288 (1)
Cl(4)	0.2807 (1)	1.0827 (3)	0.3640 (1)
P(1)	0.4770 (1)	0.8414 (2)	0.2821 (1)
P(2)	0.4410 (1)	0.6767 (2)	0.3799 (1)
P(3)	0.4045 (1)	0.9859 (2)	0.3724 (1)
Si(1)	0.2976 (1)	0.8131 (2)	0.1826 (1)
Si(2)	0.2195 (1)	0.6771 (3)	0.0566 (1)
Si(3)	0.0359 (2)	0.6585 (4)	0.1046 (1)
Si(4)	0.1530 (1)	0.6325 (3)	0.2334 (1)
O(1)	0.2832 (3)	0.7314 (7)	0.1180 (2)
O(2)	0.1155 (3)	0.6724 (8)	0.0662 (2)
O(3)	0.0799 (3)	0.6750 (7)	0.1746 (2)
O(4)	0.2525 (3)	0.7043 (6)	0.2268 (2)
N(1)	0.4664 (3)	0.6794 (5)	0.3167 (2)
N(2)	0.4023 (4)	0.8287 (6)	0.4057 (2)
N(3)	0.4350 (3)	0.9912 (5)	0.3108 (2)
C(1)	0.5975 (4)	0.8719 (7)	0.2820 (3)
C(2)	0.4246 (4)	0.8212 (7)	0.2058 (2)
C(3)	0.2443 (6)	1.0078 (9)	0.1783 (4)
C(4)	0.2283 (6)	0.8193 (15)	−0.0021 (4)
C(5)	0.2590 (8)	0.4786 (13)	0.0399 (5)
C(6)	−0.0474 (8)	0.8197 (16)	0.0834 (6)
C(7)	−0.0202 (7)	0.4715 (15)	0.0898 (5)
C(8)	0.1152 (5)	0.7231 (13)	0.2979 (3)
C(9)	0.1622 (6)	0.4171 (11)	0.2405 (5)

reaction mixture was then extracted with 3–100-mL portions of diethyl ether. The ethereal layer was dried over $MgSO_4$ and suction-filtered through Fuller's Earth, and the ether was removed under reduced pressure to yield an oil. Compound **9c** (50%)[69] was separated from **10** (50%) by preparative liquid chromatography on silica gel using a 35% CH_2Cl_2/65% hexane solvent mixture. Compound **11c** (25%) was separated from **13c** (25%) and 12 (50%) by column chromatography on silica gel, as was **13c** (50%) from 12 (50%). Compounds **9c**, **11c**, and **13c** were further purified by vacuum distillation (100–130 °C (0.05 mmHg)). Complete characterization data are given in Tables I–III.

Chlorine Replacement by CF_3CH_2ONa with PCH_2–Si Bond Cleavage: Synthesis of $N_3P_3(OCH_2CF_3)_5Me$ (10) and *gem*-$N_3P_3(OCH_2CF_3)_4Me_2$ (12). Chlorine replacement reactions with accompanying PCH_2–Si bond cleavage to yield $N_3P_3(OCH_2CF_3)_5Me$ (**10**) or *gem*-$N_3P_3(OCH_2CF_3)_4(Me)_2$ (**12**) were carried out in an identical manner. A THF solution of CF_3CH_2ONa was prepared by the careful addition of CF_3CH_2OH (5.50 g, 0.0550 mol) dissolved in THF (20 mL) to a suspension of NaH (1.20 g, 0.0500 mol) in dry THF (80 mL). On completion of hydrogen evolution, compound **1**, **2**, or **3** (0.00500 mol) was added to the CF_3CH_2ONa solution. The reaction mixture was stirred at 25 °C for 1 h followed by reflux at 66 °C for 24 h. When cooled, the reaction mixture was poured into 5% HCl (100 mL) and extracted with diethyl ether (100 mL). The ethereal layer was dried over $MgSO_4$ and suction-filtered through Fuller's Earth to give a clear solution. Evaporation of the solvent under reduced pressure yielded **10** or **12** as an oil. Species $N_3P_3(OCH_2CF_3)_5Me$ (**10**) was identified by ^{31}P NMR spectroscopy, by infrared spectral comparison with an authentic sample, and by mass spectrometry (parent ion at 645 amu). Compound **12**, *gem*-$N_3P_3(OCH_2CF_3)_4Me_2$, was recrystallized from hexane to yield a white solid. (For characterization data, see Tables I–III.) The yields of **10** and **12** were approximately 70%.

X-ray Structure Determination Technique. Our general X-ray structure technique has been described in earlier papers,[51,70] and only the details related to the present work will be given here. Crystals of **1c** and **3c** were grown by slow sublimation in evacuated (sealed at 0.05 mmHg) Pyrex glass tubes at 50–80 °C and were isomorphous. Crystals of **2c** were grown from acetonitrile solution

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[69] Approximate percentage of product in the reaction mixture as determined by ^{31}P NMR spectroscopy.

[70] Allcock, H. R.; Nissan, R. A.; Harris, P. J.; Whittle, R. R. *Organometallics* 1984, *3*, 432.

Table XII. Average Cyclotetrasiloxane Bond Distances (Å) and Bond Angles (deg)[a]

compd	bond distance		bond angles		
	Si–O	Si–C	O–Si–O	Si–O–Si	C–Si–C
2c (ring A)	1.61 (1)	1.87 (3)	109.3 (3)	150 (5)	113 (1)
2c (ring B)	1.60 (3)	1.84 (6)	110 (1)	154 (6)	109 (6)
3c	1.61 (1)	1.85 (2)	108.8 (4)	150 (7)	112 (1)
$[N_3P_3(NMe_2)_5NH(CH_2)_3]Me_7O_4Si_4$[49]	1.62 (1)	1.83 (1)	109.4 (4)	143 (3)	113 (1)
$(OSiMe_2)_4$[41]	1.65 (1)	1.92 (2)	109 (6)	143 (1)	106 (6)
$Me_6Ph_2O_4Si_4$[42]	1.631 (5)	1.851 (10)	109.5 (6)	144 (4)	112.5 (5)
$Me_4Ph_4O_4Si_4$[40]	1.62 (3)	1.84 (2)	111 (1)	149 (6)	114 (1)

[a] The standard deviation from the mean bond length or bond angle is in parentheses.

Table XIII. Summary of Crystal Data and Intensity Collection Parameters

	2c	3c
formula	$C_{16}H_{46}Cl_4N_3O_8P_3Si_8$	$C_9H_{28}Cl_4N_3O_4P_3Si_4$
fw, amu	867.8	587.3
cryst size, mm	0.27 × 0.20 × 0.07	0.36 × 0.27 × 0.22
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.002 (4)	14.847 (2)
b, Å	15.148 (3)	8.620 (2)
c, Å	15.315 (3)	22.828 (3)
α, deg	117.71 (1)	
β, deg	97.36 (1)	100.59 (1)
γ, deg	96.33 (1)	
V, Å^3	2198.6	2871.8
Z	2	4
d(calcd), g/cm^3	1.311	1.359
θ limits, deg	$2 > \theta > 20$	$2 > \theta > 25$
scan width (0.35 tan θ), deg	0.70	0.80
data collected	4074	5037
obsd data	2676	2864
μ, cm^{-1}	6.27	7.61
R, R_w	0.067, 0.082	0.055, 0.077
data/parameter ratio	7.1	11.7
empirical absorptn correctn		
min corr factor	0.948	0.987
max corr factor	1.000	1.000
largest residual peak, e Å^{-3}	1.0	1.0
av shift/error	0.2	0.1

by slow evaporation of the solvent. A summary of the important crystallographic data is presented in Table XIII.

The structures were solved by direct methods using MULTAN '82.[71] In each case, the first E map revealed the positions of all non-hydrogen atoms. Both structures were refined by full-matrix least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms. Difference Fourier syntheses, calculated toward the end of refinement, showed only a few maxima consistent with the expected positions of H atoms in both structures. Therefore, H atoms were not included in the refinement. In both structures, terminal atoms and especially the C atoms of **2c** showed large thermal motion and/or small disorder. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann.[72] At the conclusion of the refinements, the values of R and $R_w = [\sum w\Delta^2/\sum wF_o^2]$ were 0.067 and 0.082, respectively, for **2c** and 0.055 and 0.077, respectively, for **3c**. In the refinements, weights were derived from the counting statistics.

Bond lengths (Tables IV and V), bond angles (Tables VI and VII), and positional parameters (Tables VIII and IX) are given in the text. The following are available as supplementary material: selected least-squares planes and distances of atoms from those planes (Tables X and XI), thermal parameters (Tables XIV and XV), and the observed and calculated structure factor amplitudes (Tables XVI and XVII).

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Registry No. **1a**, 104738-08-1; **1b**, 104738-09-2; **1c**, 104738-10-5; **2a**, 104738-11-6; **2b**, 104738-12-7; **2c**, 104738-13-8; **3a**, 104738-14-9; **3b**, 104738-15-0; **3c**, 104738-16-1; **9a**, 104738-17-2; **9b**, 104738-18-3; **9c**, 104738-19-4; **10**, 75155-07-6; **11a**, 104738-20-7; **11b**, 104760-99-8; **11c**, 104738-21-8; **12**, 104738-25-2; **13a**, 104738-22-9; **13b**, 104738-23-0; **13c**, 104738-24-1; $(NPCl_2)_3$, 940-71-6; (chloromethyl)trimethylsilane, 2344-80-1; (chloromethyl)pentamethyldisiloxane, 17201-83-1; (chloromethyl)heptamethylcyclotetrasiloxane, 17882-66-5; (iodomethyl)trimethylsilane, 4206-67-1; (iodomethyl)pentamethyldisiloxane, 18143-98-1; (iodomethyl)heptamethylcyclotetrasiloxane, 17882-88-1; trifluoroethanol, 75-89-8.

Supplementary Material Available: Tables of selected least-squares planes and distances of atoms from those planes (Tables X and XI) and thermal parameters (Tables XIV and XV) and the stereoscopic views of **2c** (Figure 3) and **3c** (Figure 4) (9 pages); listings of the observed and calculated structure factor amplitudes (Tables XVI and XVII) (56 pages). Ordering information is given on any current masthead page.

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[71] Main, P.; Fiske, S. J.; Hull, S.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN '82, Universities of York, England, and Louvain, Belgium, 1982.

[72] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.