collection parameters, and refined details. The unit cell parameters were determined by least-squares fit of a set of 25 reflections. An absorption correction was not needed given the small value of μ (Mo Kα).

The structure was solved by the conventional Patterson method and Fourier differences. After isotropic and anisotropic refinements, hydrogen atoms were located from difference-Fourier syntheses. Full-matrix least-squares refinement of the structure (x, y, z, $\beta(i, j)$ for non-hydrogen atoms and x, y, z for hydrogen atoms) gave $R = 0.053$ and $R_W = 0.061$. Selected interatomic distances and angles are given in Table II. Final positional parameters and equivalent thermal parameters are listed in Table III. F_o and F_c values are available as supplementary material.

Acknowledgment. We are grateful to Dr. S. A. R. Knox (Bristol, U.K.) and Drs. J.-R. Hamon, J.-Y. Saillard, and S. Sinbhandit(Rennes) for helpful discussions. A gift of iron pentacarbonyl was generously provided by BASF (Ludwigshafen, West Germany).

Registry No. 1, 89875-17-2; 2, 86853-57-8; 3, 92468-51-4; *trans*-4, 105669-94-1; *cis*-4, 105814-32-2; *trans*-4a, 112339-96-5; *cis*-4a, 112318-77-1; *trans*-5, 112173-26-9; *cis*-5, 112318-76-0; 6, 82025-16-9; 8, 105698-25-7; 9, 100197-92-0; 10, 17876-91-4; 11, 112173-17-8; 12, 105669-96-3; 13, 112173-19-0; 14, 112173-21-4; 15, 112173-23-6; 15a, 112173-24-7; $[(\eta\text{-}C_5Me_5)Ru(CO)_2]_2$, 70669-56-6; Me_2PhSiH, 766-77-8; Et_3SiH, 617-86-7; Ph_3SiH, 789-25-3; C_2H_4, 74-85-1; Ph_3SiOMe, 1829-41-0; Ph_3SiMe, 791-29-7; styrene, 100-42-5.

Supplementary Material Available: Complete tables of bond lengths and angles for 15a and a table of general temperature factor expressions (3 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Alkylation of Cyclic and High Polymeric Phosphazenes via Reactions between Aluminum Alkyls and Aminophosphazenes[1,2]

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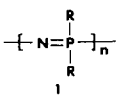
Received March 24, 1987

(Dimethylamino)chlorophosphazenes react with $(CH_3)_3Al$, $(C_2H_5)_2AlCl$, or $(C_2H_5)_3Al$ to replace chlorine atoms geminal to the amino groups by alkyl units. Subsequent treatment of these products with hydrogen chloride brings about replacement of the dimethylamino groups by chlorine. These reactions have been investigated for cyclic phosphazene trimers that bear one, two, or three dimethylamino units, for cyclic phosphazene tetramers that bear two or four dimethylamino units, and for a mixed-substituent high polymeric phosphazene substrate. Chlorine replacement by aluminum alkyls is promoted by the electron-supplying character of the amino side groups, and three plausible mechanisms are presented. Alkylation is accompanied by phosphorus–nitrogen bond cleavage during reactions that involve the high polymer. The new cyclophosphazenes were characterized by elemental analysis, mass spectrometry, and ^{31}P and ^1H NMR analysis. The high polymeric derivatives were also examined by gel permeation chromatography and differential scanning calorimetry.

A growing interest exists in the synthesis of long-chain poly(organophosphazenes) of structure 1 that contain alkyl



1

or aryl groups attached to the skeleton through phosphorus–carbon bonds.[3,4] Interest in such species is connected with their structural similarity to the well-known poly(organosiloxanes), together with the prospect that they may have special photolytic or thermal properties, or may be useful as biomedical materials.[5]

Three main synthetic pathways exist that could yield polymers of type 1. First, such species might be accessible via the reactions of high polymeric halogenophosphazenes, such as $(NPCl_2)_n$ or $(NPF_2)_n$, with organometallic reagents in a manner analogous to that already developed for the synthesis of alkoxy-, aryloxy-, or aminophosphazene high polymers.[5,6] However, the reactions of $(NPCl_2)_n$ with Grignard or organolithium reagents are often complicated by skeletal cleavage or cross-linking reactions.[2,3,7,8]

A second approach involves the ring-opening polymerization of alkyl- or arylcyclophosphazenes. Such compounds can be prepared by the reactions of main-group organometallic reagents with cyclic halogenophosphazenes.[2,9] However, so far, only cyclophosphazenes that bear *both* organic and halogeno side groups have been polymerized to the corresponding linear or macrocyclic high polymers.[10]

The third method for the synthesis of polymers of type 1 was developed by Neilson and Wisian-Neilson.[4] It involves the thermal decomposition of *P*-(trifluoroethoxy)-*N*-silylphosphinimines and has yielded a number of medium molecular weight alkyl- and arylphosphazene polymers.

(1) This paper is part of a series on phosphorus–nitrogen ring systems and high polymers. For a previous paper in this series see: Allcock, H. R.; Brennan, D. J.; Graaskamp. J. M. *Macromolecules* **1988**, *21*, 1.

(2) For a comprehensive review of the organometallic chemistry of phosphazenes see: Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*(2), 119.

(3) (a) Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 210. (b) Evans, T. L.; Patterson, D. B.; Suszko, P. R.; Allcock, H. R. *Macromolecules* **1981**, *14*, 218.

(4) (a) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848. (b) Neilson, R. H.; Wisian-Neilson, P. *J. Macromol. Sci., Chem.* **1981**, *A16*(1), 425.

(5) (a) Allcock, H. R. *Chem. Eng. New* **1985**, *63*(11), 22. (b) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Sci.* **1975**, *15*, 322.

(6) (a) Allcock, H. R. *Angew, Chem., Int. Ed. Engl.* **1977**, *16*, 147. (b) Evans, T. L.; Allcock, H. R. *J. Macromol. Sci., Chem.* **1981**, *A16*(1), 409.

(7) Allcock, H. R.; Chu, C. T.-W. *Macromolecules* **1979**, *12*, 551.

(8) Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350.

(9) (a) Allcock, H. R. *Phosphorus Sulfur* **1983**, *18*, 267. (b) Allen, C. W. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 77.

(10) (a) Allcock, H. R., Ritchie, R. J.; Harris, P. J. *Macromolecules* **1980**, *13*, 1332. (b) Allcock, H. R.; Connolly, M. S. *Macromolecules* **1985**, *18*, 1330.

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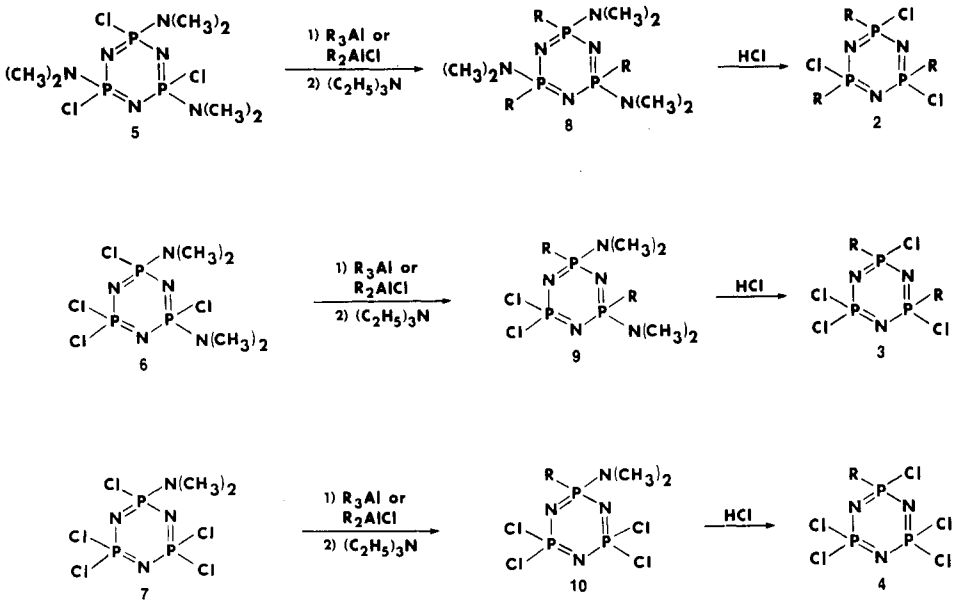
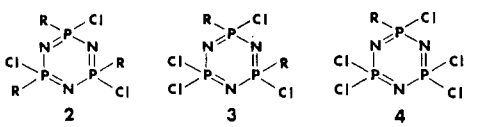
Scheme I



In this paper we focus on a pathway to the synthesis of alkylphosphazene polymers that is related to the first two methods. Specifically, we have developed an approach that allows the preparation of phosphazene cyclic trimers that bear both alkyl and halogeno side groups, and this method has been transposed to the direct reaction between a high polymeric halogenophosphazene and an organometallic reagent. In addition, the mechanisms of these reactions have been examined.

Until recently, the most direct route to the synthesis of alkylchlorocyclotriphosphazenes, such as **2–4**, was via the



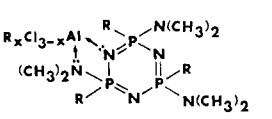
reactions of chlorocyclophosphazenes with Grignard, organocopper, or organolithium reagents.[11–13] The preparation of **2** and **3** in high yield requires the prior presence of dimethylamino side groups to direct the incoming alkyl groups to the geminal site.[11] The dimethylamino groups must then be replaced by chlorine through treatment with hydrogen chloride. This method is further complicated by an interaction between the reaction intermediates and etheric solvents to generate alkoxy derivatives. The synthesis of species of type $N_3P_3Cl_5R$ (**4**)[12] requires the use of hydridophosphazenes as intermediates,[14] and these are sensitive to air and moisture.

Harris and Jackson[15] have shown that high degrees of alkylation can be achieved by treating $(NPCl_2)_{3\text{ or }4}$ with trimethylaluminum. In this paper we report an alternative route to the synthesis of **2–4** (R = CH_3 or C_2H_5)[16] which involves reactions between aluminum alkyls and (dimethylamino)chlorocyclotriphosphazenes. Because these reactions can be carried out in toluene solvent, no opportunities for alkoxyphosphazene formation exist. The reactions between aluminum alkyls and (dimethylamino)chlorocyclo*tetra*phosphazenes were also studied. This is important because previous studies[17] have indicated that the reactivity of phosphazene high polymers is more closely modeled by cyclic tetramers than by cyclic trimers,[18] especially when organometallic reagents are involved. Finally, a preliminary study was carried out to examine the synthetic utility of this method with the use of a high polymeric phosphazene substrate.

Results and Discussion

Reactions between Aluminum Alkyls and (Dimethylamino)chlorophosphazene Cyclic Trimers. Substrates **5**, **6**, and **7** (Scheme I)[19,20] reacted with trimethylaluminum or diethylaluminum chloride, followed by triethylamine, to yield the compounds shown as **8–10** (R = CH_3 or C_2H_5). Only the chlorine atoms geminal to the dimethylamino groups were replaced by alkyl groups. The mechanistic implications of this will be discussed later. Substrates **5** and **6**, bearing three or two dimethylamino groups, required less forcing conditions for alkylation than did substrate **7** with only one dimethylamino group (see Experimental Section).

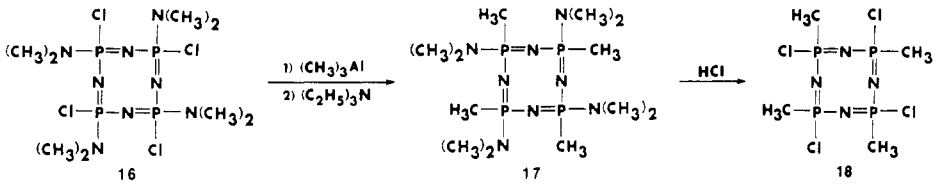
Species **8–10** could not be isolated unless the reaction mixtures were treated with triethylamine. Instead, the initial products appeared to be phosphazenylaluminum complexes of the type shown in **11**. These were detected



by ^{31}P NMR spectroscopy when **5–7** reacted with trimethylaluminum.[21] The formation of complexes such as

(11) Allcock, H. R.; Desorcie, J. L.; Wagner, L. J. *Inorg. Chem.* **1985**, *24*, 333.
(12) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844.
(13) Winter, H.; van de Grampel, J. C. *J. Chem. Soc., Dalton Trans.* **1986**, 1269.
(14) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.
(15) (a) Harris, P. J.; Jackson, L. A. *Organometallics* **1983**, *2*, 1477. (b) Jackson, L. A. Ph.D. Thesis, Virginia Polytechnic and State University, 1986.
(16) Ring-opening polymerization studies for compounds **2** and **3** (R = CH_3 or C_2H_5) are currently underway in our laboratory, and the results will be presented in a later paper. The synthesis of high molecular weight poly(organophosphazenes) derived from **4** (R = CH_3, C_2H_5, C_3H_7-*n*, C_4H_9-*n*, or C_6H_5) has already been described.
(17) (a) Allcock, H. R.; Suszko, P. R.; Evans, T. L. *Organometallics* **1982**, *1*, 1443. (b) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Whittle, R. R. *Organometallics* **1984**, *3*, 663. (c) Biddlestone, M.; Shaw, R. A. *J. Chem. Soc. A* **1970**, 1750. (d) Lavin, K. D. Ph.D. Thesis, The Pennsylvania State University, 1985.
(18) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(19) Keat, R.; Shaw, R. A. *J. Chem. Soc.* **1965**, 2215.
(20) Moeller, T.; Lanoux, S. *Inorg. Chem.* **1963**, *2*, 1061.

Scheme II



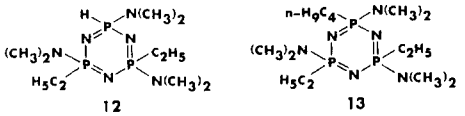
16 17 18

11 seems reasonable in view of the skeletal basicity of alkyl- and aminophosphazenes[22] and the ability of aluminum alkyl species to form complexes with amines.[23] Similar complexes are formed during reactions between alkyl Grignard reagents and aminophosphazenes.[11]

The dimethylamino groups could be displaced from 8 and 9 by treatment with hydrogen chloride in boiling toluene (Scheme I). More forcing conditions (see Experimental Section) were needed to convert the monodimethylamino derivatives (10) to 4.

The yields and physical properties of products 8–10 and 2–4 are listed in Table I. Also listed are the number of geometrical isomers detected by VPC analysis. Cis and trans isomers can exist for compounds 2, 3, 8 and 9. The trans isomer of 5 was used as the initial reaction substrate. This is the most readily obtained isomer isolated from the reaction between $(NPCl_2)_3$ and 6 equiv of dimethylamine.[19] However, substrate 6 was used as a mixture of cis and trans isomers. The proof of structure for the various products isolated is described in a later section.

Diethylaluminum chloride yielded simpler reaction mixtures than did triethylaluminum. For example, $[NP(C_2H_5)NMe_2]_3$ (8) was formed together with ≃15% of the hydridophosphazene (12) and ≃1% of the butylphosphazene (13).[24] Products 12 and 13 are probably formed from $(C_2H_5)_2AlH$ and $(C_2H_5)_2AlC_4H_9$-*n* generated during the commercial preparation of $(C_2H_5)_3Al$ from aluminum, hydrogen, and ethylene.[23]

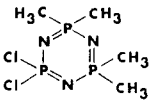


12 13

Reaction Mechanism. Why does chlorine replacement by alkyl groups occur at those phosphorus atoms in the cyclic trimer that bear a dimethylamino group at the geminal position? Three plausible explanations provide possible answers. First, the basicity and coordinating power of the side group nitrogen atoms may induce the formation of coordination adducts between alkylaluminum species and dimethylamino side groups. Interactions of this type would direct the aluminum alkyls to substitutive chlorine replacement at the geminal positions.

A second possible mechanism involves coordination between *skeletal* nitrogen atoms and aluminum alkyls. It is well-known that amino side groups enhance the basicity of the nearby skeletal nitrogen atoms by electron supply into the phosphazene ring.[22] Conceivably, this effect could favor coordination by the aluminum alkyl to a skeletal nitrogen atom rather than to a side group nitrogen.

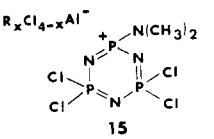
It has been reported[15] that $(NPCl_2)_3$ reacts with trimethylaluminum via a geminal-substitution route to give compound 14. Methyl side groups also raise the basicity



14

of skeletal nitrogen atoms through electron supply into the phosphazene ring, and, indeed, skeletal nitrogen atoms are the only plausible sites available for coordination in this system. However, this reaction requires relatively severe conditions, and it is not clear if an indication of skeletal coordination in this system would have any significance with respect to the dimethylamino case. It is perhaps relevant that 5–7 react with trimethyloxonium tetrafluoroborate to methylate the side groups rather than the skeletal atoms.[25]

A third mechanism can be envisaged which involves the participation by a phosphonium ion intermediate such as 15. Similar intermediates are believed to be formed during



15

Friedel–Crafts arylation reactions of cyclic halogenophosphazenes[26–28] and during aminophosphazene alkylation reactions by Grignard reagents.[11] The formation of intermediates such as 15 is expected to be favored by the presence of electron-supplying amino or alkyl groups which can stabilize the positive charge at phosphorus.

Further evidence in favor of the three mechanisms described above is provided by the relative reactivities of cyclotriphosphazenes toward chlorine replacement by aluminum alkyls. These increase in the order $(NPCl_2)_3$ < $N_3P_3Cl_5NMe_2$ < *non-gem*-$N_3P_3Cl_4(NMe_2)_2$, and *non-gem*-$N_3P_3Cl_3(NMe_2)_3$. This parallels the presumed order of increasing phosphazene basicity as well as the presumed order of increasing tendency to generate species of type 15. Thus, all three mechanism may contribute, with one or another predominating for specific phosphazene structures or reaction conditions. As will be demonstrated in the following sections, the details of the mechanism appear to change when the cyclic trimeric phosphazene system is replaced by the cyclic tetramer or high polymer.

Differences in the Behavior of Cyclic Tetrameric Phosphazenes. 1,3,5,7-Tetrakis(dimethylamino)-1,3,5,7-

(21) The ^{31}P NMR spectra of the reaction mixtures formed by treatment of $N_3P_3Cl_3(NMe_2)_3$, $N_3P_3Cl_4(NMe_2)_2$, or $N_3P_3Cl_5NMe_2$ with trimethylaluminum are believed to correspond to methylaluminum adducts of the methyl-substituted cyclotriphosphazenes: $N_3P_3(CH_3)_3(NMe_2)_3$·$(CH_3)_xCl_{3-x}Al$ (cis and trans), singlets at 37.7 and 36.4 ppm; $N_3P_3Cl_2(CH_3)_2(NMe_2)_2$·$(CH_3)_xCl_{3-x}Al$ (cis and trans), AB_2 spin systems at, A, 22.8 ppm, B, 38.8 ppm, J_{PNP} = 10.4 Hz, and A, 21.3 ppm, B, 40.1 ppm, J_{PNP} unresolved; $N_3P_3Cl_4(CH_3)NMe_2$·$(CH_3)_xCl_{3-x}Al$; AB_2 spin system at, A, 34.8 ppm, B, 22.3 ppm, J_{PNP} = 12.0 Hz.

(22) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic: New York, 1972.

(23) Mole, T.; Jeffrey, E. A. *Organoaluminum Compounds*; Elsevier: New York, 1972.

(24) Compound 12 could not be isolated, but the presence of the P–H functionality was detected from spectroscopic analysis of the product mixture: ^{31}P NMR 20.8, 18.5 ppm; ^1H NMR δ 7.26 (J_{PH} = 504 Hz); IR ν_{PH} 2280 cm^{-1}. Compound 13 was detected by vapor-phase chromatography/mass spectrometry analysis.

(25) Rapko, J. N.; Feistel, G. R. *Inorg. Chem.* **1970**, *9*, 1401.

(26) Acock, K. G.; Shaw, R. A.; Wells, F. B. G. *J. Chem. Soc. London* **1964**, 121.

(27) Das, S.; Shaw, R. A.; Smith, B. S. *J. Chem. Soc., Dalton Trans.* **1973**, 1881.

(28) Allen, C. W.; Bedell, S.; Pennington, W. T.; Cordes, A. W. *Inorg. Chem.* **1985**, *24*, 1653.

Table I. Cyclophosphazene Physical Properties and Synthesis Data

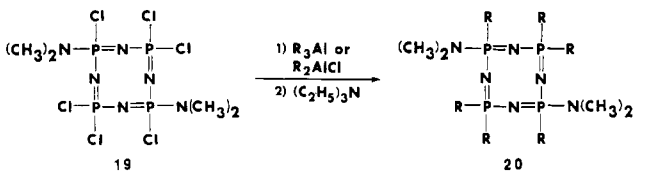
compound	% yield	bp, °C (mm), or mp, °C	no. of isomers[a]
$N_3P_3[N(CH_3)_2]_3(CH_3)_3$ (**8**)	72	97 (0.3)	2
$N_3P_3[N(CH_3)_2]_3(C_2H_5)_3$ (**8**)	73	114 (0.3)	2
$N_3P_3Cl_2[N(CH_3)_2]_2(CH_3)_2$ (**9**)	73	120 (0.3)[b]	1[c]
$N_3P_3Cl_2[N(CH_3)_2]_2(C_2H_5)_2$ (**9**)	81	122 (0.2)	1[c]
$N_3P_3Cl_4[N(CH_3)_2](CH_3)$ (**10**)	77	41–42	1
$N_3P_3Cl_4[N(CH_3)_2](C_2H_5)$ (**10**)	57	75–76	1
$N_3P_3Cl_3(CH_3)_3$ (**2**)	73	145–160	2
$N_3P_3Cl_3(C_2H_5)_3$ (**2**)	66	58–65	2
$N_3P_3Cl_4(CH_3)_2$ (**3**)	81	138–143	2
$N_3P_3Cl_4(C_2H_5)_2$ (**3**)	54	59–67	2
$N_3P_3Cl_5(CH_3)$ (**4**)	70	122–123	1
$N_3P_3Cl_5(C_2H_5)$ (**4**)	76	43–44	1
$N_4P_4[N(CH_3)_2]_4(CH_3)_4$ (**17**)	74	135 (0.4)	1[c,d]
$N_4P_4Cl_4(CH_3)_4$ (**18**)	80	135–150	3
$N_4P_4[N(CH_3)_2]_2(CH_3)_6$ (**20**)	73	107 (0.3)	1[c,e]
$N_4P_4[N(CH_3)_2]_2(C_2H_5)_6$ (**20**)	52	148 (0.1)	1[c,e]

[a] Determined by VPC analysis. [b] Compound solidified on distillation, mp 45–50 °C. [c] Two isomers were detected by ^{31}P NMR spectroscopy. [d] An isomeric mixture (three components) of **16** has been obtained from the reaction of $(NPCl_2)_4$ with 8 equiv of dimethylamine.[29] [e] Only the trans isomer of **19** is isolated when $(NPCl_2)_4$ reacts with 4 equiv of dimethylamine.[29]

tetrachlorocyclotetraphosphazene, $[NPClNMe_2)_4$ (**16**),[29] reacted with trimethylaluminum and triethylamine to yield the methylated product $[NP(CH_3)NMe_2]_4$ (**17**) (Scheme II). This compound was converted to $[NPClCH_3]_4$ (**18**) by reaction with anhydrous hydrogen chloride. However, a complex mixture of products was isolated from the attempted ethylation of **16** by $(C_2H_5)_2AlCl$.[30,31]

The reactions between $[NPClNMe_2]_4$ (**16**) and aluminum alkyls are complicated by the insolubility of the cyclotetraphosphazenyl–aluminum complexes. Two-phase reaction mixtures are generated when toluene solutions of **16** are treated with $(CH_3)_3Al$ or $(C_2H_5)_2AlCl$. In the case of $(C_2H_5)_2AlCl$, the cyclotetraphosphazene is apparently removed from solution before complete replacement of chlorine by ethyl groups can occur. The phosphazenyl-aluminum complexes of the cyclic trimer derivatives are completely soluble in toluene solution.

Suprisingly, the bis(dimethylamino)cyclotetraphosphazene derivative (**19**)[29] reacted with aluminum alkyls to replace all six chlorine atoms and yield compounds of structure **20** (R = CH_3 or C_2H_5). Even though

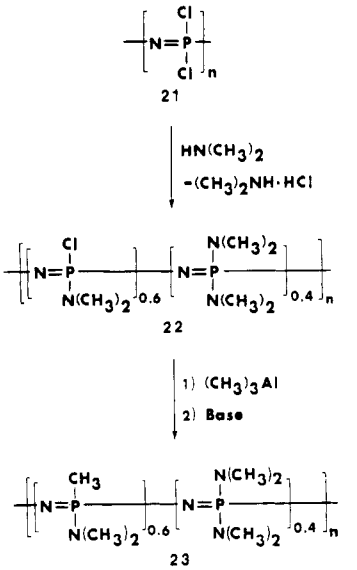


19 **20**

elevated temperatures were needed to achieve complete conversions of **19** to **20** (see Experimental Section), chlorine replacement was more than 90% complete when the reaction between **19** and $(CH_3)_3Al$ was carried out at 25 °C. Diethylaluminum chloride was significantly less reactive.

The reactivity differences between the cyclic trimers and tetramers may be related to the greater flexibility and torsional mobility of the cyclotetraphosphazene ring.[22] This would facilitate *non-geminal* chlorine replacement by aluminum alkyl species coordinated to dimethylamino side groups of cyclic tetramers. It would also expose the skeletal nitrogen atoms to adduct formation. Skeletal-nitrogen coordination may be consistent with the insolubility of the tetrameric phosphazenylaluminum complexes as well.

Scheme III



21 **22** **23**

The yields, physical properties, and number of isomers detected for the cyclotetraphosphazenes synthesized are listed in Table I. Their structural characterization will be discussed later. Four geometrical isomers are possible for compounds **17** and **18** while only two isomers can exist for **20**.[32]

Prospects for High Polymer Synthesis. As demonstrated, an extensive series of cyclic alkylphosphazenes is accessible through the reactions of aluminum alkyls with (dimethylamino)chlorophosphazenes. In addition, the mechanistic nuances detected provide a valuable insight into the structure-reactivity relationships which exist in these systems. It was, therefore, of some interest to carry out a preliminary examination of the utility of this method for the replacement of chlorine by alkyl groups through the direct reaction between a high polymeric phosphazene substrate and an alkylaluminum reagent.

Reactions involving phosphazene high polymers (and high polymers in general) are extremely sensitive to local molecular shielding, intermolecular chain coupling, and chain scission effects.[18] Hence, reaction conditions must be chosen carefully in order to minimize these problems. The reactions between *cyclic* phosphazenes and aluminum alkyls indicate that substitutive chlorine replacement occurs smoothly when $[NPClNMe_2]_n$ (n = 3 or 4) reacts with trimethylaluminum. The processes which occur during reactions that involve diethylaluminum chloride or trimethylaluminum especially with substrates that contain PCl_2 units are less clear. Therefore, the reaction between a high polymeric analogue of $[NPClNMe_2]_3$ and $(CH_3)_3Al$ represents a logical starting point for testing the efficiency of chlorine replacement by aluminum alkyls at the macromolecular level.

High polymeric $(NPCl_2)_n$ ($n \approx 15\,000$) (**21**) was allowed to react with 3 equiv[33] of dimethylamine to generate the

(29) Millington, D.; Sowerby, D. B. *J. Chem. Soc., Dalton Trans.* **1972**, 2035.

(30) Identical results were obtained when ethylaluminum dichloride was used in place of diethylaluminum chloride. Only trace amounts of cyclophosphazenes were recovered when ethylation of **16** was attempted at 80 °C.

(31) We have recently prepared and isolated the ethyl derivative of **18**, $[NPClC_2H_5]_4$, via an alternative route.

(32) Grushkin, B., Berlin, A. J.: McClanahan, J. L.; Rice, R. G. *Inorg. Chem.* **1966**, *5*, 1972.

mixed-substituent poly((dimethylamino)chlorophosphazene) (22) (Scheme III).[34] Addition of trimethylaluminum to a toluene solution of 22 resulted in precipitation of the polymer, presumably due to the formation of polymeric phosphazenylaluminum complexes. Following treatment with aqueous sodium hydroxide,[35] the mixed-substituent poly((dimethylamino)methylphosphazene) of structure 23 was isolated. Polymer 23 is a colorless, film-forming material that is soluble in benzene, toluene, and tetrahydrofuran. Elemental microanalysis data[36] indicated that ≃97% of the chlorine atoms along the backbone had been replaced and that the polymer was essentially free from residual aluminum components.

However, gel permeation chromotography (GPC) molecular weight data ($M_w = 7.1 \times 10^4$, $M_n = 8.4 \times 10^3$) for 23 indicated that skeletal phosphorus–nitrogen bond cleavage occurred during preparation or isolation.[37] Significantly higher molecular weights ($M_w = (1.7\text{–}3.7) \times 10^6$) are found for poly(organophosphazenes) prepared by the reaction of $(NPCl_2)_n$ with sodium alkoxides or aryloxides.[38,39] The mixed-substituent substrate 22 could not be analyzed by GPC because of the presence of hydrolytically sensitive P–Cl bonds, but its intrinsic viscosity of 3.4 dL/g[40] is consistent with values obtained for other high molecular weight derivatives.[38,41] Thus, the reaction between 22 and $(CH_3)_3Al$ (and/or subsequent product isolation[37]) leads to a reduction in the average polyphosphazene chain length from ≃12000 to ≃600 repeating units (i.e. one skeletal cleavage every 600 repeating units). At the cyclic trimer or tetramer level, skeletal cleavage of this magnitude would be undetectable.

It seems likely that the formation of phosphazenylaluminum complexes not only assists the chlorine replacement process but promotes skeletal degradation by trimethylaluminum as well.[42] Similar interactions, which involve skeletal nitrogen atoms, are believed to lead to chain scission when $(NPCl_2)_n$ or $(NPF_2)_n$ reacts with organolithium reagents.[3,7,8] Thus, the mechanisms of chlorine substitution and skeletal P–N bond cleavage appear to be closely related, and it may be difficult to "uncouple" these processes by altering the organometallic reagent, phosphazene substrate, or other conditions. Thus, a more feasible method for preparing alkyl-substituted poly(organophazenes) involves the ring-opening polymerization of cyclic derivatives such as those prepared in this study. Some results from such experiments have been reported,[8,10] and others will be described in future papers.[16]

Cyclic and Polymeric Phosphazene Structural Characterization. All the cyclic compounds prepared in this study were characterized by a combination of mass spectrometry (low and high resolution), elemental microanalysis, infrared spectroscopy, and ^{31}P and ^{1}H NMR spectroscopy. These data are listed in Tables II–IV. In addition to the elemental microanalysis and molecular weight data described earlier, polymers 22 and 23 were characterized by infrared spectroscopy, ^{31}P and ^{1}H NMR spectroscopy, and differential scanning calorimetry (DSC).

The parent ion mass spectral data for the cyclic compounds synthesized are listed in Table II.[11,12] In each case, the correct parent ion was detected. Compounds 2, 3, 4, 9, 10, and 18 also generated the expected chlorine isotope pattern. The elemental analysis data are presented in Table II.

The infrared spectra for all the organophosphazenes were consistent with the proposed structures. An intense absorbance existed between 1150 and 1220 cm^{-1} for the cyclotriphosphazenes and between 1230 and 1300 cm^{-1} for the cyclotetraphosphazenes. This is a characteristic of the skeletal structure of cyclophosphazenes.[22] Other bands were detected for C–H, P–C, and P–Cl absorbances. Polymers 22 and 23 yielded broad absorbances centered at 1310 and 1250 cm^{-1}, respectively.

The proton decoupled ^{31}P NMR data for the cyclic and polymeric phosphazenes are listed in Table III. The ^{31}P NMR data for compounds 2, 3, 4, and 8 are reported elsewhere.[11,12] The spectra of cyclotriphosphazenes 9 and 10 were interpreted as AB_2 spin systems. Both cis and trans isomers were detected for compounds 9 (R = CH_3 or C_2H_5). The ^{31}P spectra of cyclotetraphosphazenes 17 and 18 are complex due to the PNP coupling interactions that arise from the various isomers. The spectra recorded for compounds of structure 20 (R = CH_3 or C_2H_5) were interpreted as A_2B_2 spin systems. The chemical shift assignments were determined from selected proton-decoupling experiments. Irradiation of the alkyl substituent protons resulted in a significantly greater broadening of ^{31}P NMR resonances assigned to $PRNMe_2$ groups relative to those assigned to PR_2 groups. This is due to unresolved phosphorus–proton coupling. The opposite effect occurred when the dimethylamino protons were irradiated. The ^{31}P NMR spectra of 22 and 23 consisted of resonances that were readily assigned to $PClNMe_2$, $P(NMe_2)_2$, and $P(CH_3)NMe_2$ groups.

The organic side groups of the cyclic and polymeric organophosphazenes were identified by inspection of the high-field ^{1}H NMR spectra of these compounds. These data are listed in Table IV. The ^{1}H NMR data for compounds 2, 3, 4, and 8 are reported elsewhere.[11,12]

The glass transition temperatures (T_g) of 22 and 23 were measured by DSC analysis and were found to be 2 and −24 °C, respectively. The T_g of 22 is not significantly different from that measured for poly[bis(dimethylamino)phosphazene] (−4 °C).[41] The lower T_g detected for 23 is most

(33) Fifty percent of the dimethylamine consumed during this reaction (1.5 equiv) functions as an acceptor for liberated hydrogen chloride.

(34) Cyclic model compound studies[18,29] suggest that a phosphazene high polymer of structure $[NPClNMe_2]_n$ should be accessible via the aminolysis of $[NPCl_2]_n$, but meticulous control of the reaction stoichiometry and conditions would be needed. Thus, it seemed that 22 was a better substrate for carrying out preliminary reactions with $(CH_3)_3Al$ since the conditions employed during its preparation would remove all traces of $NPCl_2$ units that might hinder complete chlorine replacement by the organometallic reagent.

(35) Treatment with triethylamine also solubilized the polymer, but the product 23 could not be purified thoroughly due to the insolubility of the triethylamino–aluminum complexes.

(36) Anal. Calcd for $C_{14}H_{42}N_{12}P_5Cl_3$ (22): C, 26.27; H, 6.57; N, 26.27; Cl, 16.65. Found: C, 26.21; H, 6.43; N, 26.09; Cl, 16.98. Anal. Calcd for $C_{17}H_{51}N_{12}P_5$ (23): C, 35.29; H, 8.82; N, 29.07. Found: C, 34.84; H, 8.71; N, 29.12; Cl, 0.43; Al, 0.01.

(37) Skeletal degradation may result from basic hydrolysis of residual P–Cl bond during product isolation. However, cyclic model compound studies indicate that aminophosphazenes are, in general, quite stable to strong base: Allcock, H. R.; Fuller, T. J.; Matsumura, K. *Inorg. Chem.* **1982**, *21*, 515.

(38) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

(39) Austin, P. E.; Riding, G. H.; Allcock, H. R. *Macromolecules* **1983**, *16*, 719.

(40) The intrinsic viscosity, [η], was measured on a solution of 22 in THF at 25 °C.

(41) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.

(42) A reviewer suggested that the behavior of the polymer $[NP(NMe_2)_2]_n$ with Me_3Al might indicate whether chain cleavage was associated with the presence of P–Cl bonds in macromolecules such as 22. Unfortunately, $[NP(NMe_2)_2]_n$ is insoluble in toluene or similar hydrocarbon solvents. However, the related piperidino-substituted polymer, $[NP(NC_5H_{10})_2]_n$, is soluble in toluene, and this compound was treated with Me_3Al. The interaction resulted in precipitation of the polymer, presumably, as its trimethylaluminum adduct. Isolation of the products by the same methods as used for 23 yielded a polymer with a similar molecular weight to that of the starting material. This suggests (but does not prove) that the chain cleavage found with 22 is perhaps associated more with the halogen substitution process than with the coordination step.

Table II. Cyclophosphazene Mass Spectral and Elemental Analysis Data

compound	low and high resolution mass spectrum				elemental anal.		
	found	calcd	found	calcd		found	calcd
$N_3P_3[N(CH_3)_2]_3(CH_3)_3$ (8)	*a*	*a*	*a*	*a*	C	34.42	34.62
					H	8.80	8.65
					N	26.58	26.92
$N_3P_3)N(CH_3)_2]_3(C_2H_5)_3$ (8)	*a*	*a*	*a*	*a*	C	40.14	40.68
					H	9.27	9.32
					N	23.76	23.73
$N_3P_3Cl_2[N(CH_3)_2]_2(CH_3)_2$ (9)	323[b]	323	323.0154	323.0152	C	22.39	22.22
					H	5.48	5.56
					N	21.56	21.60
$N_3P_3Cl_2[N(CH_3)_2]_2(C_2H_5)_2$ (9)	351[b]	351	351.0465	351.0465	C	27.17	27.27
					H	6.55	6.25
					N	19.75	19.89
$N_3P_3Cl_4[N(CH_3)_2](CH_3)$ (10)	334[c]	334	333.8772	333.8794	C	10.99	10.71
					H	2.86	2.68
					N	16.57	16.67
$N_3P_3Cl_4[N(CH_3)_2](C_2H_5)$ (10)	348[c]	348	347.8950	347.8951	C	13.87	13.71
					H	3.28	3.14
					N	15.75	16.00
$N_3P_3Cl_3(CH_3)_3$ (2)	*a*	*a*	*a*	*a*	C	12.77	12.57
					H	3.07	3.14
					N	14.62	14.67
$N_3P_3Cl_3(C_2H_5)_3$ (2)	*a*	*a*	*a*	*a*	C	22.06	21.93
					H	4.78	4.57
					N	12.80	12.79
$N_3P_3Cl_4(CH_3)_2$ (3)	*a*	*a*	*a*	*a*	C	8.19	7.82
					H	1.93	1.96
					N	13.15	13.68
$N_3P_3Cl_4(C_2H_5)_2$ (3)	*a*	*a*	*a*	*a*	C	14.18	14.35
					H	3.11	3.02
					N	12.39	12.55
$N_3P_3Cl_5(CH_3)$ (4)	*d*	*d*	*d*	*d*	C	4.12	3.66
					H	1.07	0.92
					N	12.84	12.82
$N_3P_3Cl_5(C_2H_5)$ (4)	*d*	*d*	*d*	*d*	C	7.22	7.03
					H	1.66	1.46
					N	12.33	12.30
$N_4P_4[N(CH_3)_2]_4(CH_3)_4$ (17)	416	416	416.2020	416.2013	C	34.82	34.62
					H	8.52	8.65
					N	27.01	26.92
$N_4P_4Cl_4(CH_3)_4$ (18)	380[c]	380	379.8757	379.8767	C	12.89	12.57
					H	3.11	3.14
					N	14.69	14.67
$N_4P_4[N(CH_3)_2]_2(CH_3)_6$ (20)	358	358	358.1485	358.1482	C	33.49	33.52
					H	8.44	8.38
					N	23.31	23.46
$N_4P_4[N(CH_3)_2]_2(C_2H_5)_6$ (20)	442	442	442.2429	442.2421	C	43.22	43.44
					H	9.53	9.50
					N	19.16	19.00

[a] See ref 11. [b] Cl_2 isotope pattern. [c] Cl_4 isotope pattern. [d] See ref 12.

likely a consequence of the reduced molecular weight of this material.

Experimental Section

Materials. (Dimethylamino)chlorocyclophosphazenes (**5**, **6**, **7**, **16**, and **19**)[19,20,29] and poly(dichlorophosphazene) (**21**)[39] were prepared by using published procedures. Aluminum alkyls were obtained commercially from Aldrich as 1.8–2.0 M solutions in toluene. Toluene was distilled into the reaction flask under an atmosphere of dry argon from a sodium benzophenone ketyl agent. Triethylamine (Aldrich) was used as received. Anhydrous hydrogen chloride (Matheson, electronic grade) was passed through a trap at −78 °C before being introduced into the reaction flask. Dimethylamine (Matheson) was dried over sodium before use. All reactions involving aluminum alkyls were carried out under an atmosphere of dry argon.

Analytical Equipment and Techniques. ^{31}P NMR spectra were recorded with the use of JEOL FX-90Q spectrometer operating at 36 MHz. Positive chemical shifts are downfield from external phosphoric acid. ^1H NMR spectra were recorded with the use of a Bruker WP-200 spectrometer operating at 200 MHz. Chemical shifts are relative to tetramethylsilane at δ 0. Infrared spectra were recorded on a Perkin-Elmer 283B spectrometer. The samples were prepared as thin films (NaCl disks) or KBr pellets. Electron-impact mass spectral data were obtained with the use of an AEI MS 950 spectrometer. VPC analyses were carried out by using a Varian 3700 gas chromatograph equipped with a flame ionization detector and a 2-m SP2100 (3%) column. Gel permeation chromatography (GPC) data were obtained with the use of a Hewlett-Packard HP 1090 liquid chromatograph equipped with a refractive index detector. Polymer Laboratories PLgel (10^6, 10^6, 10^3 Å) columns were calibrated with narrow molecular weight polystyrene standards. A 0.1% $(n\text{-}C_4H_9)_4NBr$ solution in THF was employed as the eluent. Intrinsic viscosities were measured with an Ubbelohde viscometer (Cannon) in a thermoregulated water bath. Glass transition temperatures (T_g) were recorded with the use of a Perkin-Elmer DSC 7 equipped with a PE 7500 computer. The samples (10–20 mg) were analyzed in crimped aluminum pans with a heating rate of 10 °C/min and a helium flow rate of 10 mL/min. The instrument was calibrated with a cyclohexane standard with thermal transitions at −87.06 and 6.54 °C. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN 37921.

Synthesis of $N_3P_3R_3(NMe_2)_3$ (8), $N_3P_3Cl_2R_2(NMe_2)_2$ (9), and $N_4P_4(CH_3)_4(NMe_2)_4$ (17). These reactions were all carried out in a similar manner. The following procedure is typical. To a solution of $N_3P_3Cl_3(NMe_2)_3$ (**5**) (25 g, 0.067 mol) in toluene (500

Table III. Cyclic and Polymeric Phosphazene ^{31}P NMR Data[a]

compound	chemical shift (ppm)				coupling const, Hz
$N_3P_3Cl_2[N(CH_3)_2]_2(CH_3)_2$ (9)	P(N)(C)	30.4	$P(Cl)_2$	19.6	J_{PNP} = 12.7
	P(N)(C)	29.7	$P(Cl)_2$	20.0	J_{PNP} = 14.7
$N_3P_3Cl_2[N(CH_3)_2]_2(C_2H_5)_2$ (9)	P(N)(C)	35.5	$P(Cl)_2$	21.0	J_{PNP} = 9.8
	P(N)(C)	35.2	$P(Cl)_2$	20.5	J_{PNP} = 9.8
$N_3P_3Cl_4[N(CH_3)_2](CH_3)$ (10)	P(N)(C)	30.6	$P(Cl)_2$	19.5	J_{PNP} = 17.6
$N_3P_3Cl_4[N(CH_3)_2](C_2H_5)$ (10)	P(N)(C)	36.7	$P(Cl)_2$	20.0	J_{PNP} = 10.7
$N_4P_4[N(CH_3)_2]_4(CH_3)_4$ (17)	P(N)(C)	17.9			
	P(N)(C)	16.7			
$N_4P_4Cl_4(CH_3)_4$ (18)	P(N)(Cl)	18.3			
	P(N)(Cl)	17.6			
	P(N)(Cl)	10.8			
$N_4P_4[N(CH_3)_2]_2(CH_3)_6$ (20)	P(N)(C)	19.6	$P(C)_2$	14.0	
	P(N)(C)	18.5	$P(C)_2$	15.9	
$N_4P_4[N(CH_3)_2]_2(C_2H_5)_6$ (20)	P(N)(C)	20.5	$P(C)_2$	21.1	
	P(N)(C)	18.9	$P(C)_2$	23.1	
$[(NPCl[N(CH_3)_2])_{0.6}(NP[N(CH_3)_2]_2)_{0.4}]_n$ (22)	P(N)(Cl)	−13.0	$P(N)_2$	0.7	
$[(NP[N(CH_3)_2](CH_3))_{0.6}(NP[N(CH_3)_2]_2)_{0.4}]_n$ (23)	P(N)(C)	2.7	$P(N)_2$	0.7	

[a] Cyclic phosphazene spectra were recorded for a solution of the compound in $CDCl_3$. Polymeric phosphazene spectra were recorded for a solution of the compound in C_6D_6.

Table IV. Cyclic and Polymeric Phosphazene ^1H NMR Data[a,b]

compd	signal	chem shift (δ)	coupling const, Hz
$N_3P_3Cl_2[N(CH_3)_2]_2(CH_3)_2$ (9)	$-N(CH_3)_2$	2.66 (d)	J_{PNCH} = 12.2
		2.65 (d)	J_{PNCH} = 12.8
	$-CH_3$	1.62 (d)	J_{PCH} = 14.6
		1.61 (d)	J_{PCH} = 14.7
$N_3P_3Cl_2[N(CH_3)_2]_2(C_2H_5)_2$ (9)	$-N(CH_3)_2$	2.65 (d)	J_{PNCH} = 11.6
	$-CH_2CH_3$	1.76 (m)	
	$-CH_2CH_3$	1.14 (d, t)	J_{PCCH} = 20.8
			J_{HCCH} = 7.6
$N_3P_3Cl_4[N(CH_3)_2](CH_3)$ (10)	$-N(CH_3)_2$	2.67 (d)	J_{PNCH} = 13.1
	$-CH_3$	1.69 (d, t)	J_{PCH} = 15.9
			J_{PNPCH} = 2.0
$N_3P_3Cl_4[N(CH_3)_2](C_2H_5)$ (10)	$-N(CH_3)_2$	2.67 (d)	J_{PNCH} = 12.5
	$-CH_2CH_3$	1.88 (m)	
	$-CH_2CH_3$	1.19 (d, t)	J_{PCCH} = 22.1
			J_{HCCH} = 7.5
$N_4P_4[N(CH_3)_2]_4(CH_3)_4$ (17)	$-N(CH_3)_2$	2.58 (d)	J_{PNCH} = 11.2
	$-CH_3$	1.33 (d)	J_{PCH} = 14.5
		1.29 (d)	J_{PCH} = 13.4
$N_4P_4Cl_4(CH_3)_4$ (18)	$-CH_3$	2.00 (m)	
$N_4P_4[N(CH_3)_2]_2(CH_3)_6$ (20)	$-N(CH_3)_2$	2.61 (d)	J_{PNCH} = 11.1
		2.60 (d)	J_{PNCH} = 11.1
	$-CH_3$	1.46 (m)	
$N_4P_4[N(CH_3)_2]_2(C_2H_5)_6$ (20)	$-N(CH_3)_2$	2.65 (d)	J_{PNCH} = 9.9
		2.63 (d)	J_{PNCH} = 10.1
	$-CH_2CH_3$	1.63 (m)	
	$-CH_2CH_3$	1.08 (m)	
$[(NPCl[N(CH_3)_2])_{0.6}(NP[N(CH_3)_2]_2)_{0.4}]_n$ (22)	$-N(CH_3)_2$	2.80 (m)	
$[(NP[N(CH_3)_2](CH_3))_{0.6}(NP[N(CH_3)_2]_2)_{0.4}]_n$ (23)	$-CH_3$	1.64 (d)	J_{PCH} = 13.7

[a] Cyclic phosphazene spectra were recorded for a solution of the compound in $CDCl_3$. Polymeric phosphazene spectra were recorded for a solution of the compound in C_6D_6. [b] Abbreviations d, doublet; t, triplet; m, unresolved multiplet.

mL) was added $(CH_3)_3Al$ (125 mL of a 2.0 M solution in toluene) dropwise over a period of 60 min. The solution was stirred at 25 °C for 16 h. The reaction mixture was then exposed to the atmosphere for 24 h. After this time, 2-propanol (100 mL) was added slowly to destroy unreacted alkylaluminum reagent. The mixture was then diluted with hexane (1000 mL), and triethylamine (100 mL) was added to precipitate aluminum salts. The mixture was filtered, the solvent was removed under reduced pressure, and the residue was extracted with hexane. Filtration and solvent removal yielded the product as a colorless oil that was purified by vacuum distillation.

Synthesis of $N_3P_3Cl_4RNMe_2$ (10). The following procedure is typical. To a solution of $N_3P_3Cl_5NMe_2$ (7) (50 g, 0.14 mol) in toluene (500 mL) was added $(CH_3)_3Al$ (100 mL of a 2.0 M solution in toluene) over a period of 30 min. The solution was then heated at 80 °C for 16 h. The reaction mixture was allowed to cool to 25 °C and was exposed to the atmosphere for 24 h. After this time, 2-propanol (80 mL) was added slowly to destroy unreacted alkylaluminum reagent. The mixture was then diluted with hexane (1000 mL), and triethylamine (80 mL) was added to precipitate aluminum salts. Filtration and solvent removal yielded the product as a white solid which was purified by recrystallization from hexane.

Synthesis of $N_3P_3Cl_3R_3$ (2), $N_3P_3Cl_4R_2$ (3), and $N_4P_4Cl_4(CH_3)_4$ (18). All these reactions were carried out in a similar manner, and the following procedure is typical. A solution of $N_3P_3(CH_3)_3(NMe_2)_3$ (8) (R = CH_3) (35 g, 0.11 mol) in toluene (300 mL) was heated to reflux. Anhydrous hydrogen chloride was then bubbled through the solution for 2 (R = CH_3) or 4 h (R = C_2H_5). At the end of this time, the solution was allowed to cool to 25 °C and the precipitated dimethylamine hydrochloride was removed by filtration. The solvent was removed under reduced pressure. The residue was extracted with methylene chloride, and the solution was filtered through neutral alumina. Solvent removal yielded the product as a white solid which was purified by recrystallization from heptane (R = CH_3) or hexane (R = C_2H_5).

Synthesis of $N_3P_3Cl_5R$ (4). The following procedure is typical. A Pyrex tube (25 mm o.d. × 400 mm length) fitted with a Teflon Fischer-Porter valve was charged with $N_3P_3Cl_4(CH_3)NMe_2$ (10, R = CH_3) (15 g, 0.045 mol). Anhydrous hydrogen chloride gas (4.2 L, 0.11 mol) was then condensed into the tube at −196 °C. The sealed tube was then heated in an oil bath at 120 °C for 16 h. (*Caution*: Precautions should be taken to guard against pressure-induced shattering of the glass tube.) The tube was then removed from the oil bath and allowed to cool to 25 °C, and the contents were extracted with toluene. The insoluble dimethylamine hydrochloride was removed by filtration, and the solvent was removed under reduced pressure. The residue was extracted with methylene chloride, and the solution was filtered through neutral alumina. Solvent removal yielded the product as a white solid which was purified by recrystallization from hexane.

Reaction between 5 and $(C_2H_5)_3Al$. To a solution of $N_3P_3Cl_3(NMe_2)_3$ (5) (25 g, 0.067 mol) in toluene (500 mL) was added $(C_2H_5)_3Al$ (150 mL of a 1.9 M solution in toluene) dropwise over a period of 60 min. The solution was stirred at 25 °C for 16 h. The reaction mixture was then exposed to the atmosphere for 24 h. After this time, 2-propanol (125 mL) was added to destroy any unreacted alkylaluminum reagent. The mixture was then diluted with hexane (1000 mL), and triethylamine (125 mL) was added to precipitate aluminum salts. The mixture was filtered, the solvent was removed under reduced pressure, and the residue was extracted with hexane. Filtration and solvent removal yielded a colorless oil (22.4 g). VPC analysis indicated that, in addition to 8 (R = C_2H_5), the product mixture consisted of two other components with shorter and longer retention times. These are believed to correspond to 12 and 13, respectively.[24]

Synthesis of $N_4P_4R_6(NMe_2)_2$ (20). These reactions were carried out in an identical manner. For example, a solution of $N_4P_4Cl_6(NMe_2)_2$ (19) (15 g, 0.031 mol) in toluene (500 mL) was heated to 80 °C. Trimethylaluminum (125 mL of a 2.0 M solution in toluene) was then added dropwise over a period of 60 min. The solution was stirred at 80 °C for 16 h. The reaction mixture was then allowed to cool to 25 °C and was exposed to the atmosphere

for 24 h. 2-Propanol (100 mL) was then added slowly to destroy unreacted alkylaluminum reagent. The solvent was then removed under reduced pressure, and the residue was extracted with methylene chloride. Triethylamine (100 mL) was added and the solution was filtered through neutral alumina. The solvent was removed, and the residue was extracted with hexane. Filtration and solvent removal yielded the product as a colorless oil which was purified by vacuum distillation.

Synthesis of $[(NPClNMe_2)_{0.6}(NP(NMe_2)_2)_{0.4}]_n$ (22). Into a solution of $(NPCl_2)_n$ (**21**) (20 g, 0.17 mol) in toluene (1200 mL) was condensed dimethylamine (35 mL, 0.53 mol) over a period of 4 h. The solution was stirred for 16 h. The precipitated dimethylamine hydrochloride was removed by filtration through a medium-frit under an atmosphere of dry argon followed by washing with additional toluene (300 mL). The combined toluene solutions were then degassed to remove unreacted dimethylamine. The final volume was 1300 mL. This solution was stored in an inert-atmosphere drybox and was used for further reactions with trimethylaluminum. Polymer **22** was isolated for characterization following removal of the toluene solvent under reduced pressure.

Synthesis of $[NP(CH_3)NMe_2)_{0.6}(NP(NMe_2)_2)_{0.4}]_n$ (23). To a solution of **22** in toluene (830 mL), prepared as described above, was added $(CH_3)_3Al$ (80 mL of a 2.0 M solution in toluene) dropwise over a period of 60 min. The polymer precipitated from solution, and stirring was continued for an additional 16 h. After this time, the reaction mixture was cooled to 0 °C and NaOH (600 mL of a 1.0 M aqueous solution) was added slowly to destroy unreacted alkylaluminum reagent. The organic and aqueous layers were decanted, and the polymer was dissolved in a mixture of THF (800 mL) and NaOH (600 mL of a 1.0 M aqueous solution). The organic layer was collected and concentrated to ≃100 mL. The product was isolated following centrifugation. Purification by reprecipitation (3×) from THF into water yielded 10.1 g of **23**.

Acknowledgment. This work was supported by the Office of Naval Research. We thank Ethyl Corp. for a gift of hexachlorocyclotriphosphazene, D. J. Brennan for obtaining the GPC data, and J. M. Graaskamp for obtaining the DSC data.

Registry No. **2** (R = CH_3), 32997-23-2; **2** (R = C_2H_5), 112137-47-0; **3** (R = CH_3), 112069-20-2; **3** (R = C_2H_5), 112069-21-3; **4** (R = CH_3), 71332-21-3; **4** (R = C_2H_5), 71332-23-5; **5**, 3721-13-9; **6**, 2203-74-9; **7**, 1078-85-9; **8** (R = CH_3), 66621-95-2; **8** (R = C_2H_5), 112137-46-9; **9** (R = CH_3), 112069-16-6; **9** (R = C_2H_5), 112069-17-7; **10** (R = CH_3), 112069-18-8; **10** (R = C_2H_5), 112069-19-9; **12**, 112069-25-7; **13**, 112069-26-8; **16**, 28049-39-0; **17**, 112069-22-4; **18**, 33193-09-8; **19**, 92276-63-6; **20** (R = CH_3), 112069-23-5; **20** (R = C_2H_5), 112069-24-6; **21**, 26085-02-9.

Generation of Mercury and Cadmium Cationic Complexes from Oxidation Processes Observed in the Presence of Dimethylmercury and Dimethylcadmium at Mercury, Platinum, and Glassy Carbon Electrodes

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Received May 18, 1987

Electrochemical oxidation processes at mercury, platinum, and glassy carbon electrodes in the presence of Me_2Hg generate a mercury-rich cationic complex that is believed to be $[Me_2Hg_3]^{2+}$ or a closely related species. At mercury electrodes, direct participation of the electrode is involved in the electrochemical reaction, which is postulated to occur according to $Me_2Hg + 2Hg \rightarrow [Me_2Hg_3]^{2+} + 2e^-$. Reduction of the mercury-rich cation $[Me_2Hg_3]^{2+}$ at a platinum electrode leads to deposition of elemental mercury and regeneration of Me_2Hg at the mercury-plated platinum electrode: $[Me_2Hg_3]^{2+} + 2e^- \rightarrow Me_2Hg + 2Hg$. At platinum and glassy carbon electrodes, $[Me_2Hg_3]^{2+}$ is also produced as a product of controlled potential electrolysis experiments. In this case, the initially generated $[Me_2Hg]^+$ complex is formed at very positive potentials. $[Me_2Hg]^+$ then reacts rapidly to generate the cationic methyl mercury complex. The overall process at platinum and glassy carbon electrodes is proposed as $3Me_2Hg \rightarrow [Me_2Hg_3]^{2+} + 4Me^\bullet + 2e^-$. Oxidation processes associated with the presence of Me_2Cd are also electrode-dependent. At mercury electrodes, alkyl and metal exchange occurs via a bimetallic alkylcadmium–mercury intermediate: $Me_2Cd + Hg \rightarrow Me_2Hg + Cd^{2+} + 2e^-$. At platinum and glassy carbon electrodes the reaction occurs at more positive potentials than at mercury electrodes and generates inorganic cadmium ions: $Me_2Cd \rightarrow Cd^{2+} + 2Me^\bullet + 2e^-$.

Introduction

The chemical and physical properties of alkylated mercury and cadmium compounds have been widely studied.[1,2] Dimethylcadmium is highly reactive and used in organic synthesis as a methylating reagent.[1] Dimethylmercury is far more stable and exists even in water for considerable periods of time.[3] Consequently, dimethylmercury and its more stable monomethyl derivatives are of considerable environmental importance, and their presence in marine food chains has been linked to localized poisonings of human populations.[1,3,4]

While a great deal is known about the chemical reactions and toxicity of dimethylcadmium and dimethylmercury, very little is known about their redox properties. As far

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