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Synthesis of 1-Halo- and 1-Alkyl-1-phenyltetrachlorocyclotriphosphazene Polymerization "Monomers" from Bi(cyclophosphazenes)

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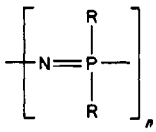
A new synthetic route has been developed for the preparation of 1-halo- and 1-alkyl-1-phenyltetrachlorocyclotriphosphazenes of general formula $N_3P_3Cl_4X(C_6H_5)$ (**5**), where X = Cl, Br, or I, and $N_3P_3Cl_4(C_6H_5)(R)$ (**6**), where R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *i*-C_3H_7, or $CH_2CH{=}CH_2$, respectively. These compounds are prospective polymerization monomers, most of which cannot be prepared by other routes. The synthetic procedure involves the interaction of 1,1′-diphenyl-3,3,3′,3′,5,5,5′,5′-octachlorobi(cyclotriphosphazene) (**2**) with $LiBEt_3H$ to give a triethylborane-substituted anion, **3**. Anion **3** reacts with proton-releasing agents to give 1-hydrido-1-phenyltetrachlorocyclotriphosphazene (**4**) or with alkyl halides to give **6**. The hydridophosphazene **4** reacts with halogen in CCl_4 to give **5**. Alternatively, compounds **5** (X = Cl, Br) can be prepared via the reaction of **3** with CCl_4 or $CHBr_3$, respectively. Compound **5** (X = Br) was found to react with NaF in acetonitrile at reflux to give exclusively $N_3P_3Cl_4F(C_6H_5)$. The structural characterization of these compounds by spectroscopic and mass spectrometric techniques is discussed, together with the reaction mechanism. In addition, the crystal and molecular structure of **5** (X = Cl) has been investigated by single-crystal X-ray diffraction techniques. The crystals are monoclinic with the space group $P2_1/c$ and with a = 8.579 (1) Å, b = 14.612 (3) Å, c = 11.771 (3) Å, and β = 99.26 (1)° with V = 1456.4 (9) Å^3 and Z = 4.

Considerable interest exists in the development of new synthesis routes to both cyclic and high polymeric phosphazenes (**1**) that contain alkyl or aryl groups bonded to



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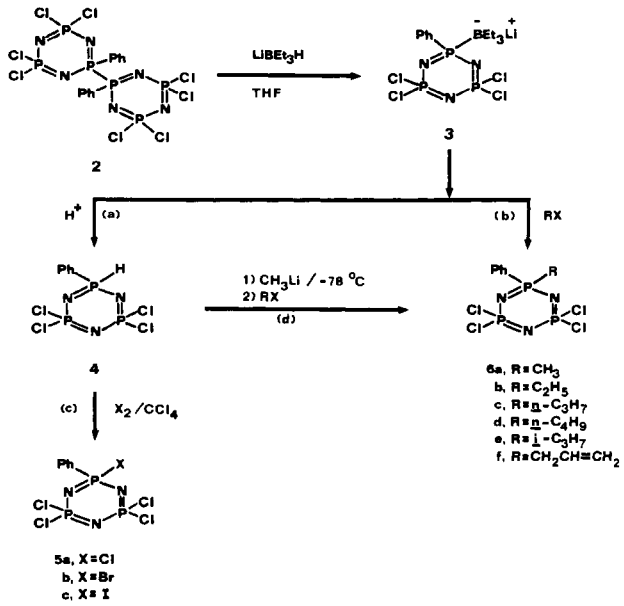
the inorganic skeleton through P–C bonds.[1-17] Linear high polymeric species of this type are expected to be more resistant to high-temperature thermal rearrangement or fragmentation than the well-known analogues with P–O or P–N bonded side groups. Moreover, the presence of alkyl or aryl groups bonded directly to the skeleton should change the inter- and intramolecular interactions which, in turn, would modify the solid state physical properties.

Scheme I



A condensation–polymerization route has been developed by Neilson and Wisian-Neilson[12a,b] that allows the synthesis of poly(alkylphosphazenes) of type **1**. However, high polymeric aryl derivatives have not yet been prepared by that route.[12c] Our approach is to synthesize phosphazene cyclic trimers that bear the requisite alkyl or aryl groups, together with halogen substituents, and to examine the polymerization behavior of these cyclic species. In this way, the prospect exists that high polymers with a range of alkyl, aryl, alkoxy, aryloxy, and/or amino substituents on the same chain may become accessible. This approach

(1) For a previous paper in this series, see: Allcock, H. R.; Connolly, M. S.; Harris, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 2482.
(2) Allcock, H. R. *Polymer.* **1980**, *21*, 673.
(3) Harris, P. J.; Desorcie, J. L.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1981** 852. Allcock, H. R.; Desorcie, J. L.; Harris, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 2814.
(4) Allcock, H. R.; Ritchie, R.; Harris, P. J. *Macromolecules* **1981**, *13*, 1332.
(5) Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 2256.
(6) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.
(7) Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350.
(8) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844.
(9) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.
(10) Allcock, H. R.; Chu, T.-W. *Macromolecules* **1979**, *12*, 551.
(11) Allcock, H. R.; Patterson, D. B.; Evans, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6095.
(12) (a) Neilson, R. H.; Wisian-Neilson, P. *J. Am. Chem. Soc.* **1980**, *102*, 2848. (b) Neilson, R. H.; Wisian-Neilson, P. *J. Macromol. Sci., Chem.* **1981**, *A16* (1), 425. (c) Phenylphosphazene polymers have been prepared by the condensation route,[12b] but no molecular weight data were reported.
(13) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.
(14) Biddlestone, M.; Shaw, R. A. *J. Chem. Soc. A* **1969**, 178; **1970**, 1750; **1971**, 2715.
(15) Allen, C. W.; Toch, P. L. *Inorg. Chem.* **1981**, *20*, 8.
(16) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(17) Ramachandran, K.; Allen, C. W. *J. Am. Chem. Soc.* **1982**, 104, 2396.

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might allow the synthesis of linear macromolecules with a precisely controlled sequencing of several different substituents along the chain.

Earlier we reported the preparation of 1,1-dialkyltetrachlorocyclotriphosphazenes[6] and 1-alkylpentachlorocyclotriphosphazenes.[8] These latter species can be polymerized thermally.[4] However, efforts to prepare phenyl-substituted analogues or phenyl alkyl derivatives by the treatment of $(NPCl_2)_3$ with phenyllithium, phenylmagnesium chloride, phenylcopper, or phenyl cuprate were unsuccessful.[18]

The synthesis of bi(cyclophosphazenes) (compounds with phosphazene rings linked through a P–P bond), with each phosphorus atom at the linkage site bearing an alkyl or aryl group, was described recently.[1,3] These compounds react with nucleophiles, such as sodium trifluoroethoxide or sodium phenoxide, to yield new organocyclotriphosphazenes.[1] Thus, the prospect existed that cleavage of the P–P bond with other nucleophiles such as lithium triethylborohydride might provide a route to hitherto inaccessible monophenylcyclotriphosphazenes. In this paper, we describe this new synthesis route. The polymerization behavior of the cyclophosphazenes will be discussed in another paper.

Results and Discussion

Overall Reaction Sequence. The reaction sequence is shown in Scheme I. The phenyl-substituted bi(cyclophosphazene) **2** can be prepared by the reaction between hexachlorocyclotriphosphazene, $(NPCl_2)_3$, and phenylmagnesium chloride in tetrahydrofuran (THF) solvent.[1,3] Compound **2** was found to react with 2 equiv of $LiBEt_3H$ in THF at 0 °C to give the triethylborane-substituted phosphazene anion **3**. This intermediate was not isolated from the reaction mixture, but its structure was confirmed by ^{31}P NMR analysis (see later).

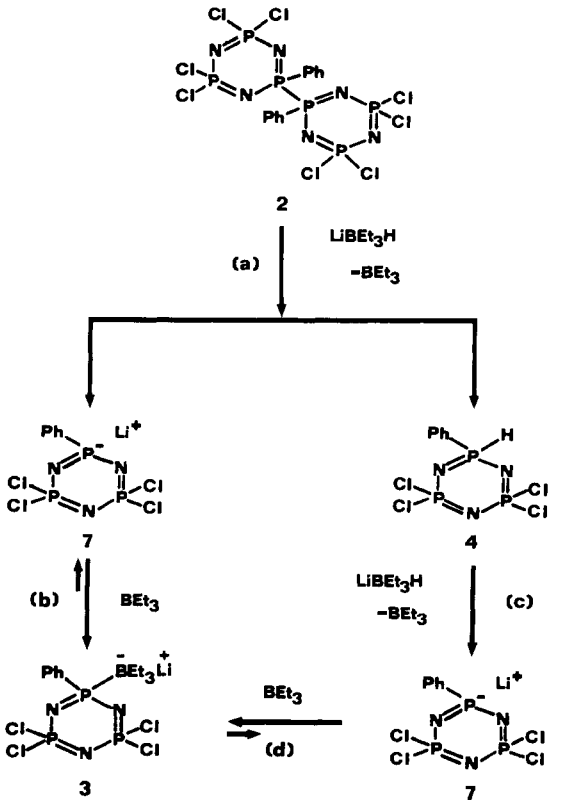
Phosphazene anion **3** reacted with proton-releasing reagents to yield 1-hydrido-1-phenyltetrachlorocyclotriphosphazene (**4**). This compound was isolated as an air- and moisture-sensitive, white, crystalline material. Treatment of **4** with excess halogen in carbon tetrachloride gave the 1-halo-1-phenyltetrachlorocyclotriphosphazenes (**5**) in which the halogen, X, was chlorine, bromine, or iodine. Of these, only the iodo derivative was unstable during several days exposure to the atmosphere.

The triethylborane-substituted anion **3** was also found to react with several alkyl halides to yield 1-alkyl-1-phenyltetrachlorocyclotriphosphazenes, **6**. Compounds **6** were isolated where R was CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, and $CH_2CH{=}CH_2$. These products were air- and moisture-stable, white, crystalline, volatile materials.

Compounds **6** were also prepared (where R = CH_3, n-C_4H_9, or $CH_2CH{=}CH_2$) by the interaction of **4** with methyllithium in THF at −78 °C, followed by treatment with alkyl halide (pathway d in Scheme I). The overall yields of compounds **6** were much lower by this route because of the need to isolate **4** as part of the sequence. Thus, pathway b has a higher practical value. However, pathway d provides a clue to the reaction mechanism involved, as outlined later.

Mechanism of P–P Bond Cleavage. It might be supposed that the reaction of the bi(cyclophosphazene) **2** with 1 equiv of $LiBEt_3H$ would give initially a phosphazene anion (**7**) and a hydridophosphazene (**4**) (Scheme II, pathway a). Neither intermediate was detected by ^{31}P NMR spectroscopy during the course of the reaction.

Scheme II



However, the triethylborane-substituted phosphazene anion **3** was detected as a stable intermediate. Therefore, we propose that species **7** (a Lewis base) reacts rapidly with triethylborane (a Lewis acid) to give the phosphazene anion **3**. The hydridophosphazene intermediate **4** reacts with 1 equiv of $LiBEt_3H$ to generate **7**, which interacts with triethylborane to yield another molecule of anion **3** (Scheme II, pathway c plus d). The evidence for this mechanism is as follows.

First, bi(cyclophosphazenes) are known to react with nucleophiles such as sodium alkoxides or aryl oxides to give organocyclotriphosphazenes and phosphazene anions.[1] In this reaction, the nucleophile H^- reacts with the P–P bond to generate a substituted phosphazene (**4**) and a phosphazene anion (**7**).

Second, phosphazene anions such as **7** are known to be unstable at temperatures above −60 °C but are capable of "capturing" electrophiles at ambient temperatures before decomposition to yield intact phosphazene rings.[1,5] The electron-rich anion **7** must react with the electrophile triethylborane or necessarily decompose under the reaction conditions.

Third, as illustrated in Scheme I, the phosphazene anion **3** reacts with various electrophiles RX to give compounds of general formula $N_3P_3Cl_4(C_6H_5)(R)$. The yields of these compounds are more than 50%; thus, the reaction must generate two intact reactive phosphazene intermediates from each bi(cyclophosphazene) molecule consumed.

Fourth, the phosphazene anion **7** was generated at 0 °C *in the presence* of triethylborane from the reaction between an authentic sample of **4** (prepared via pathway a of Scheme I) and methyllithium. This reaction led instantly to the quantitative formation of the triethylborane-substituted anion **3**.

Finally, the hydridophosphazene **4** (prepared by pathway a of Scheme I) was found to react with $LiBEt_3H$ to give exclusively **3**.

However, our results do not distinguish between the

(18) Allcock, H. R.; Harris, P. J.; Connolly, M. S., unpublished results.

Table I. Characterization Data

compound	yield,[a] %	mp, °C	mass spectral data[29] found	mass spectral data[29] calcd	elemental anal.[25] found	elemental anal.[25] calcd
$N_3P_3Cl_4(Ph)(H)$ (4)	45	68-70	352	353	C 20.53 H 1.87 N 11.73 P 25.89 Cl 39.74	C 20.31 H 1.70 N 11.84 P 26.19 Cl 39.96
$N_3P_3Cl_5Ph$ (5a)	30[b] (55)[c]	55	387	387	C 18.56 H 1.31 N 10.97 Cl 45.75 386.8136	C 18.51 H 1.29 N 10.79 Cl 45.53 386.8139
$N_3P_3Cl_4Br(Ph)$ (5b)	25[b] (44)[c]	67	431	431	C 16.74 H 1.15 N 9.65 Br 18.13	C 16.61 H 1.16 N 9.69 Br 18.42
$N_3P_3Cl_4I(Ph)$ (5c)	17[b]	88 dec	479	479	C 15.39 H 1.22 N 8.67 I 26.10	C 14.99 H 1.05 N 8.74 I 26.40
$N_3P_3Cl_4F(Ph)$ (5d)	14[d]	oil	371	371	370.8422	370.8435
$N_3P_3Cl_4(Ph)(CH_3)$ (6a)	79[e] (65)[f] [30][g]	86	367	367	366.8682	366.8686
$N_3P_3Cl_4(Ph)(C_2H_5)$ (6b)	84[e] (43)[f]	59	381	381	380.8848	380.8842
$N_3P_3Cl_4(Ph)(n\text{-}C_3H_7)$ (6c)	85[e] (73)[f]	96	395	395	394.9000	394.8998
$N_3P_3Cl_4(Ph)(n\text{-}C_4H_9)$ (6d)	87[e] (71)[f] [34][g]	112	409	409	408.9160	408.9154
$N_3P_3Cl_4(Ph)(i\text{-}C_3H_7)$ (6e)	82[e] (36)[f]	63	395	395	394.8990	394.8998
$N_3P_3Cl_4(Ph)(C_3H_5)$ (6f)	90[e] (72)[f] [32][g]	62	393	393	392.8848	392.8842
$N_3P_3Cl_4(i\text{-}C_3H_7)_2$ (8)	65[h]	oil	361	361	360.9164	360.9155

[a] All yields, except for 8, were based on the bi(cyclophosphazene) 2. [b] Yield of the product derived from 2 and 4 (Scheme I, pathways a and c), after recrystallization. These yields were based on a 45% yield of 4. [c] Yield of the product from the reaction of 3 and CCl_4 or $CHBr_3$, after recrystallization. [d] Based on a 25% yield of 5b. [e] Yield of product derived from 2 (Scheme I, pathway b), after filtration of a solution in CH_2Cl_2 through neutral alumina. [f] Yield of product, after further purification by sublimation and recrystallization. [g] Yield of product derived from 2 and 4 (Scheme I, pathways a and d), after recrystallization. [h] Yield based on $N_3P_3Cl_4(i\text{-}C_3H_7)(H)$,[9] after sublimation.

reaction of the bi(cyclophosphazene) 2 or the hydridophosphazene 4 with $LiBEt_3H$ to give 7, followed by the reaction of 7 with triethylborane to give 3, and the concerted reaction of 2 or 4 with $LiBEt_3H$ to give 3.

Reactivity of the Phosphazene Anion 3. As described previously, 3 was found to react with a variety of alkyl halides. The reaction of 3 with methyl iodide proceeds at 25 °C during 48 h, but the other reactions required elevated temperatures (36–72 h at 66 °C). All the reactions were quantitative, as deduced by ^{31}P NMR spectroscopy (see Proof of Structure) and the yields of 6 were high (see Table I). The anion did not react with $t\text{-}C_4H_9Br$ to give a compound of type 6. This reflects the increased difficulty of nucleophilic reaction at a tertiary carbon center, presumably due to steric constraints. The higher reaction temperatures necessary for the reaction of 3 with most of the alkyl halides could suggest that an equilibrium exists between the triethylborane-substituted anion and the "free" phosphazene anion 7 (see Scheme II, pathway b or d), and that the anion 7 is the "reactive" species. This theory is supported by the fact that species 6 can be prepared from 4 via the route shown in pathway d of Scheme I. Furthermore, we have found that, when 2 reacts with $LiBEt_3H$ and methyl iodide in the presence of *excess* triethylborane, only 36% of 3 is converted to 6. The reaction was quantitative in the absence of excess triethylborane.

The fact that anion 3 is stable at elevated temperatures for up to 72 h (for example, until the reaction with an alkyl halide such as $i\text{-}C_3H_7I$ is complete), is remarkable. This stability makes these anions much more synthetically useful than the copper–phosphazene anions reported previously.[6] The copper–phosphazene compounds are unreactive toward secondary alkyl halides, and their reactivity toward primary halides is dependent on the electron-donating ability of the alkyl group bound to the phosphazene. The observation that compound 3 possesses an electron-withdrawing phenyl group and yet is still active in alkyl halide substitutions must reflect a greater reactivity, probably connected with an equilibrium involving 7. The prospect existed, therefore, that alkyl-substituted anions such as 3 could be prepared and used as intermediates in the synthesis of more sterically hindered dialkylphosphazenes than those described.[6]

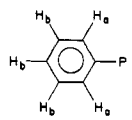
This prospect was investigated by the preparation of the hydridophosphazene $N_3P_3Cl_4(i\text{-}C_3H_7)(H)$[9] and by the reaction of it with $LiBEt_3H$ to give the anion $N_3P_3Cl_4(i\text{-}C_3H_7)(^-BEt_3Li^+)$. Addition of $i\text{-}C_3H_7I$ to the reaction mixture, followed by heating at reflux for 72 h, gave $N_3P_3Cl_4(i\text{-}C_3H_7)_2$. This compound could not be prepared via copper–phosphazene intermediates[6] and illustrates the greater reactivity of these novel anions.

Other phosphazene anions have been found to abstract Cl^+ from CCl_4 to generate P–Cl bonds.[1] The ability of 3 to undergo such a reaction would provide a convenient synthesis route to 5a. Phosphazene anion 3 was found to react with CCl_4 to give an improved yield of 5a over that obtained via pathways a and c in Scheme I. Furthermore, 3 was found to abstract Br^+ from $CHBr_3$ to give 5b. This latter abstraction reaction does not appear to have been reported previously. These routes avoid the difficulty and lower overall yield associated with the isolation and production of 4.

Phosphazene anion 3 was also found to react with hexachlorocyclotriphosphazene, $(NPCl_2)_3$. This reaction gave 5a and 2 as products. The formation of these compounds is consistent with a mechanism in which the anion abstracts Cl^+ from $(NPCl_2)_3$ to give 5a, followed by reaction of 5a with additional 3 to give the ring-coupled product 2. This type of reaction mechanism has been detected for

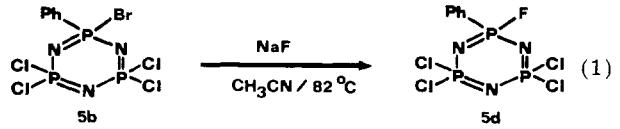
Table II. NMR Data[a]

compound	^{31}P NMR, ppm P(Ph)(R)	^{31}P NMR, ppm PCl_2	^{1}H NMR,[b] δ		coupling const,[c] Hz
$N_3P_3Cl_4(Ph)(^-BEt_3Li^+)$ (3)	72.8	7.4			J_{PNP} = 74.4
$N_3P_3Cl_4(Ph)(H)$ (4)	6.9	18.2	C_6H_5 (a)	7.83 (m)	J_{PH} = 579
			C_6H_5 (b)	7.60 (m)	J_{PNPH} = 14.5
			H	7.89 (d, m)	J_{PNP} = 10.3
$N_3P_3Cl_5Ph$ (5a)	28.9	21.2	C_6H_5 (a)	7.97 (m)	J_{PNP} = 15.5
			C_6H_5 (b)	7.60 (m)	
$N_3P_3Cl_4Br(Ph)$ (5b)	15.3	21.1	C_6H_5 (a)	7.91 (m)	J_{PNP} = 8.6
			C_6H_5 (b)	7.57 (m)	
$N_3P_3Cl_4I(Ph)$ (5c)	−23.9	20.6	C_6H_5 (a)	7.91 (m)	
			C_6H_5 (b)	7.50 (m)	
$N_3P_3Cl_4F(Ph)$ (5d)	23.8	22.4	C_6H_5 (a)	7.90 (m)	J_{PF} = 1003
			C_6H_5 (b)	7.62 (m)	J_{PNP} = 34.1
$N_3P_3Cl_4(Ph)(CH_3)$ (6a)	28.3	18.2	CH_3	1.85 (d, t)	J_{PCH} = 14.6
			C_6H_5 (a)	7.84 (m)	J_{PNP} = 10.5
			C_6H_5 (b)	7.54 (m)	J_{PNPCH} = 2.4
$N_2P_3Cl_4(Ph)(CH_2CH_3)$ (6b)	34.0	18.7	CH_2CH_3	1.23 (d, t)	J_{PCCH} = 21.4
			CH_2CH_3	1.97 (m)	J_{HCCH} = 7.5
			C_6H_5 (a)	7.83 (m)	
			C_6H_5 (b)	7.56 (m)	
$N_3P_3Cl_4(Ph)(n\text{-}C_3H_7)$ (6c)	31.9	18.5	$CH_2CH_2CH_3$	1.05 (t, d)	J_{HCCH} = 7.3
			$CH_2CH_2CH_3$	1.70 (m)	J_{PCCCH} = 1.1
			$CH_2CH_2CH_3$	1.93 (m)	
			C_6H_5 (a)	7.82 (m)	
			C_6H_5 (b)	7.55 (m)	
$N_3P_3Cl_4(Ph)(n\text{-}C_4H_9)$ (6d)	32.3	18.4	$CH_2CH_2CH_2CH_3$	0.93 (t)	J_{HCCH} = 7.2
			$CH_2CH_2CH_2CH_3$	1.47 (m)	
			$CH_2CH_2CH_2CH_3$	1.63 (m)	
			$CH_2CH_2CH_2CH_3$	1.94 (m)	
			C_6H_5 (a)	7.83 (m)	
			C_6H_5 (b)	7.55 (m)	
$N_3P_3Cl_4(Ph)(i\text{-}C_3H_7)$ (6e)	38.0	18.6	$CH(CH_3)_2$	1.13 (d, d)	J_{PCCH} = 20.1
			$CH(CH_3)_2$	2.05 (d, m)	J_{HCCH} = 7.0
			C_6H_5 (a)	7.82 (m)	J_{PCH} = 3.7
			C_6H_5 (b)	7.55 (m)	
$N_3P_3Cl_4(Ph)(CH_2CH{=}CH_2)$ (6f)	28.6	18.8	$CH_2CH{=}CH_2$	2.79 (m)	
			$CH_2CH{=}CH_2$	5.32 (m)	
			$CH_2CH{=}CH_2$	5.80 (m)	
			C_6H_5 (a)	7.84 (m)	
			C_6H_5 (b)	7.55 (m)	
$N_3P_3Cl_4(i\text{-}C_3H_7)_2$ (8)	56.6	18.8	$CH(CH_3)_2$	1.19 (d, d)	J_{PCCH} = 18.6
			$CH(CH_3)_2$	2.08 (d, m)	J_{PNP} = 7.4
					J_{HCCH} = 7.0
					J_{PCH} = 3.7

[a] All data recorded for solutions in $CDCl_3$, except for 3, which was recorded in THF. [b]  [c] Coupling constants that are not listed were unresolved.

the reactions of $(NPCl_2)_3$ with Grignard reagents.[3]

Other Reactions. The halophosphazene **5b** was found to react with 1 equiv of sodium fluoride in boiling acetonitrile to give exclusively $N_3P_3Cl_4F(C_6H_5)$ (**5d**) (eq 1).



(1)

Sodium fluoride is known to react rapidly with P–Cl bonds under these reaction conditions. Therefore, this reaction demonstrates that, when a deficiency of a nucleophilic reagent is used, the halogen replacement reaction occurs geminal to the substituent group already present. This influence was reported previously.[8]

Proof of Structure. Phosphazene anion **3** was not isolated. However, its structure was inferred from the following observations. First, the ^{31}P NMR spectrum of **3** was interpreted as an AB_2 spin system. The resonance for the phosphorus atom bound to the phenyl and triethylboron groups was found at 72.8 ppm. This marked downfield shift is similar to that observed for other phosphazene anions or for phosphazenes in which a metal is bound to the ring via a direct P–M bond.[5,19,20] Second, this resonance was broadened (see Figure 1b) because of unresolved couplings. This might be expected if the phosphorus atom is bound to boron. Third, a similar triethylborane-substituted anion was proposed as a product from the reaction of a μ-dithio compound with $LiBEt_3H$.[21,22] Conversion of anion **3** to the hydrido derivative (**4**) and to the alkyl derivatives (**6**) provided a secondary means of structure proof.

Hydridophosphazene **4** was identified by the presence of strong infrared absorbances[23,24] in the 1100–1300 cm^{-1}

(19) Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 717.
(20) Allcock, H. R.; Wagner, L. J.; Levin, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 1321.
(21) Seyferth, D.; Henderson, R. S.; Song, L.-C. *J. Organomet. Chem.* **1980**, *192*, C1.
(22) Seyferth, D.; Song, L.-C.; Henderson, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 5103.

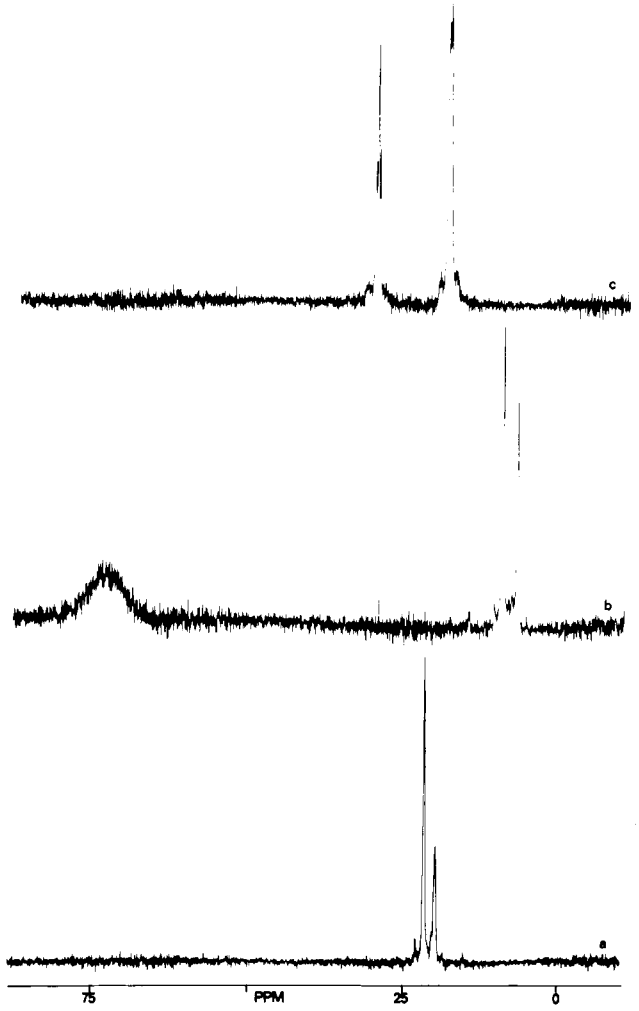


Figure 1. ^{31}P NMR spectral changes following the addition of $LiBEt_3H$ and methyl iodide to a solution of **2** in THF at 0 °C. Spectrum a was obtained from the reaction mixture of **2** in THF at 25 °C. Spectrum b was obtained after addition of $LiBEt_3H$ at 0 °C and after reaction for 24 h. Spectrum c was obtained 48 h after the addition of methyl iodide.

region (P–N ring) and a medium intensity absorbance at 2420 cm^{-1} (P–H stretch), by microanalysis,[25] and from ^1H and ^{31}P NMR spectra.[26,27] For example, the proton-decoupled ^{31}P NMR spectrum was interpreted as an AB_2 spin system.[28] The proton-undecoupled ^{31}P NMR spectrum showed the A resonance split into a doublet (J_{PH} = 579 Hz), with additional unresolved fine structure from PNP couplings. In the phosphorus-undecoupled ^1H NMR spectrum, the hydride resonance appeared as a doublet (J_{PH} = 579 Hz) with additional fine structure from the PNPH coupling. Additional proof of structure was obtained by the conversion of species **4** to species **5a** by treatment with chlorine. A parent ion was not observed in the mass spectrum (electron impact or chemical ionization).[29] Instead, an intense ion was observed for the parent minus one fragment, presumably from facile loss of a proton during analysis.

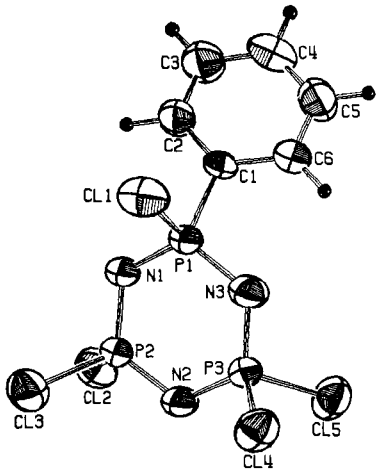


Figure 2. An ORTEP plot of the molecular structure and notation system of **5a**.

The cyclic trimers **5**, **6**, and **8** were identified by a combination of ^1H and ^{31}P NMR spectroscopy and mass spectrometry (low and high resolution), and, in representative cases, by elemental analysis. The presence of the phosphazene ring was confirmed by strong absorbances in the 1100–1300-cm^{-1} IR region. Other bands could be assigned to C–H and P–Cl vibrations. The proton-decoupled ^{31}P NMR spectra were interpreted as simple AB_2 spin systems for **5**, **6**, and **8**. The A resonance in the proton-undecoupled ^{31}P NMR spectra was broadened due to unresolved P···H coupling. For **5d**, the A resonance was split into a doublet due to P–F coupling (J_{PF} = 1003 Hz). Compounds **5a**, **5d**, **6**, and **8** yielded a parent ion in the mass spectrum, with a characteristic chlorine isotope pattern. Compounds **5b** and **5c** yielded no detectable parent ion in the mass spectrum under electron-impact mass spectrometric conditions. However, chemical ionization mass spectral analysis (with the use of methane as a carrier gas) revealed a strong parent ion (plus proton), with a characteristic Cl_4Br and Cl_4 isotope pattern, respectively.

(23) Infrared spectra for compounds **4–6** and **8** were recorded on a Perkin-Elmer 580 or 283B infrared spectrometer. Samples were used in the form of KBr disks.

(24) Infrared spectral data for compounds **4–6** and **8** are as follows. **4** (KBr): 3050 w (ν(CH)); 2420 m (ν(PH)); 1225 vs, 1180 vs, 1155 s (ν(PN)); 580 vs, 510 vs, 505 s cm^{-1} (ν(PCl)). **5a** (KBr): 3060 w (ν(CH)); 1200 vs, 1185 sh (ν(PN)); 580 s, 520 s, 485 s cm^{-1} (ν(PCl)). **5b** (KBr): 3060 vw, 3040 vw (ν(CH)); 1200 vs (ν(PN)); 585 s, 530 s, 510 s, 480 s cm^{-1} (ν(PCl), ν(Br)). **5c** (KBr): 3060 vw, 3040 vw (ν(CH)); 1180 vs, 1160 vs, 1155 vs (ν(PN)); 600 s, 580 s, 520 s, 490 s, 475 s cm^{-1} (ν(PCl), ν(PI)). **5d** (KBr): 3060 w (ν(CH)); 1235 vs, 1230 vs, 1200 vs, 1135 m (ν(PN)); 590 s, 525 sh, 510 s (ν(PCl), ν(PF)). **6a** (KBr): 3060 vw, 3050 vw, 2990 w, 2910 m (ν(CH)); 1220 vs, 1205 vs, 1190 vs, 1175 vs (ν(PN)); 565 vs, 530 vs, 515 vs, 490 m cm^{-1} (ν(PCl)). **6b** (KBr): 3080 vw, 3070 vw, 2980 w, 2940 w, 2920 w, 2880 w (ν(CH)); 1220 vs, 1185 sh, 1170 vs, 1125 m (ν(PN)); 575 vs, 520 vs, 510 sh, 485 s cm^{-1} (ν(PCl)). **6c** (KBr): 3080 vw, 3060 vw, 2970 w, 2930 w, 2910 vw, 2870 w (ν(CH)); 1250 s, 1210 vs, 1180 s, 1125 m (ν(PN)); 580 vs, 525 s, 515 sh, 485 vs cm^{-1} (ν(PCl)). **6d** (KBr): 3040 vw, 2950 m, 2920 m, 2900 vw, 2860 vw (ν(CH)); 1230 s, 1205 vs, 1165 vs, 1120 m (ν(PN)); 570 m, 510 s cm^{-1} (ν(PCl)). **6e** (KBr): 3080 vw, 3070 vw, 2970 m, 2920 w, 2900 w, 2880 w (ν(CH)); 1215 vs, 1175 vs, 1160 s, 1125 s (ν(PN)); 575 vs, 520 sh, 515 vs, 495 vs cm^{-1} (ν(PCl)). **6f** (KBr): 3080 w, 3050 w, 3020 vw, 3010 vw, 2980 vw, 2940 w, 2900 w, 2880 w (ν(CH)); 1240 s, 1200 vs, 1180 sh, 1170 vs, 1120 m (ν(PN)); 605 m, 580 s, 565 s, 510 s, 490 s cm^{-1} (ν(PCl)). **8** (KBr): 2960 m, 2930 w, 2910 sh, 2870 w (ν(CH)); 1260 m, 1230 sh, 1215 vs, 1190 sh, 1170 vs (ν(PN)); 600 m, 575 sh, 570 s, 515 s, 495 m (ν(PCl)).

(25) Microanalyses were obtained by Galbraith Laboratories, Inc., Knoxville, Tenn.

(26) ^1H NMR spectra were recorded on a Bruker WP-200 spectrometer operating at 200 MHz in the Fourier transform mode. The data were processed by using the computer contained within the WP-200 spectrometer. All data are for samples in $CDCl_3$. Positive chemical shifts were downfield from tetramethylsilane at δ 0.

(27) ^{31}P NMR spectra were recorded on a Varian CFT-20 spectrometer operating at 32 MHz in the Fourier transform mode. The data were processed by using the computer contained within the CFT-20 spectrometer. All spectra were recorded for samples in $CDCl_3$, except for **3** which was recorded in THF. Positive chemical shifts were downfield from external phosphoric acid.

(28) Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969.

(29) Electron-impact mass spectral data were obtained with the use of an AEI-MS-902 spectrometer. Chemical ionization mass spectral data were obtained with the use of a Finnigan 3200 mass spectrometer, using methane as a carrier gas.

Table III. Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for the Non-Hydrogen Atoms of $N_3P_3Cl_5C_6H_5$ (5a)

Bond Distances

Cl(1)-P(1)	2.021 (2)	P(1)-N(1)	1.590 (4)	C(1)-C(2)	1.362 (6)
Cl(2)-P(2)	1.986 (2)	P(1)-N(3)	1.587 (4)	C(1)-C(6)	1.375 (6)
Cl(3)-P(2)	1.989 (2)	N(1)-P(2)	1.554 (3)	C(2)-C(3)	1.375 (7)
Cl(4)-P(3)	1.989 (2)	N(3)-P(3)	1.559 (4)	C(3)-C(4)	1.346 (7)
Cl(5)-P(3)	1.983 (2)	P(2)-N(2)	1.575 (4)	C(4)-C(5)	1.386 (7)
C(1)-P(1)	1.778 (4)	P(3)-N(2)	1.568 (4)	C(5)-C(6)	1.368 (7)

Bond Angles

N(1)-P(1)-N(3)	117.3 (2)	C(1)-P(1)-Cl(1)	103.5 (2)	Cl(3)-P(2)-N(2)	108.5 (2)
N(1)-P(2)-N(2)	118.8 (2)	Cl(1)-P(1)-N(1)	106.5 (2)	Cl(4)-P(3)-N(2)	107.9 (2)
N(2)-P(3)-N(3)	119.2 (2)	Cl(1)-P(1)-N(3)	107.4 (2)	Cl(4)-P(3)-N(3)	109.4 (2)
P(1)-N(1)-P(2)	121.6 (2)	Cl(2)-P(2)-N(1)	109.6 (2)	Cl(4)-P(3)-Cl(5)	101.9 (1)
P(2)-N(2)-P(3)	120.9 (2)	Cl(2)-P(2)-N(2)	107.7 (2)	Cl(5)-P(3)-N(2)	108.6 (2)
P(1)-N(3)-P(3)	121.6 (2)	Cl(2)-P(2)-Cl(3)	100.8 (1)	Cl(5)-P(3)-N(3)	108.5 (2)
C(1)-P(1)-N(1)	111.1 (2)	Cl(3)-P(2)-N(1)	109.9 (2)	C-C-C (av)	120.0 (4)
C(1)-P(1)-N(3)	109.9 (2)				

Identification of the intermediates and products formed from pathway b of Scheme I was accomplished by following the changes in the ^{31}P NMR spectra of the reaction mixtures. Thus, as shown in Figure 1, the reaction of **2** with $LiBEt_3H$, followed by addition of methyl iodide, was monitored. Peaks centered at 20.7 and 18.9 ppm (Figure 1a) were assigned to PCl_2 and P(P)(Ph) resonances, respectively, in **2**. After the addition of $LiBEt_3H$ and after 24-h reaction, resonances appeared corresponding to P(Ph)($^-BEt_3Li$) and PCl_2 at 72.8 and 7.4 ppm (Figure 1b), respectively, for **3**. After the addition of methyl iodide and after stirring at 25 °C for 48 h, resonances at 30.0 and 18.4 ppm appeared (Figure 1c), which were consistent with the formation of **6a**. Although the reaction conditions were varied (see Experimental Section), all reactions of **3** with the various alkyl halides lead to the quantitative formation of **6**, as deduced from the ^{31}P NMR spectra of the reaction solutions. The surprising absence of side reactions is evident from the NMR spectra.

Crystal and Molecular Structure of 5a. A single-crystal X-ray structure determination of **5a** was carried out for several reasons. First, while the spectroscopic characterization data, mass spectral data, and elemental analysis for this material were compatible with structure **5a** (Scheme I), it was necessary to fully confirm the structure. Second, crystal structures have been reported for the 1,1-diphenyl-,[30] 1,1,3,3-tetraphenyl-,[31] and 1,1,3,3,5,5-hexaphenyl-substituted[32] cyclotriphosphazenes. Comparable data for **5a** were needed to test several unusual bonding features of phenyl-substituted cyclotriphosphazenes.[30-32] Finally, a need existed for a comparison of the detailed structural parameters of alkylpentachloro- and this phenylpentachlorocyclotriphosphazene.

The general structure of **5a** is shown in Figure 2, together with the notation system used for all non-hydrogen atoms. Bond distances and angles are listed in Table III. The phosphazene ring was found to be slightly nonplanar (χ^2 = 507 for the weighted least-squares plane through the phosphazene ring). The ring adopts a conformation such that a plane exists through P(1), P(3), N(2), and N(3) (χ^2 = 6 for the weighted least-squares plane through these atoms), and the atoms P(2) and N(1) deviate from this plane by −0.051 (1) and 0.054 (4) Å, respectively. A phenyl group and a chlorine atom are bound to phosphorus atom P(1), and two chlorine atoms are linked to each of the remaining phosphorus atoms. The dihedral angle between the plane of the phosphazene ring and the plane of the phenyl ring is 46.8°. It is likely that the orientation of the phenyl group could result from van der Waals interactions between N(3) and H(6). The distance N(3)···H(6) was 2.573 (4) Å, considerably shorter than the sum of the van der Waals radii for these atoms (2.7 Å). As a result, the distance N(1)···H(6) is longer than the sum of the van der Waals radii and was found to be 2.882 (3) Å. No reason exists for unequal nitrogen–hydrogen interactions; therefore crystal packing forces could also be involved.

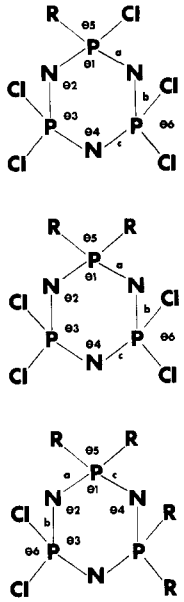


Figure 3. Bond length and angle designations for mono-, gem-di-, and gem-tetrasubstituted cyclophosphazenes.

Three different P–N bond lengths were found in the skeletal ring of **5a** (Figure 3). The P–N bonds alternate in average bond length at increasing distances from P(1), with PN(a) = 1.588 (2) Å, PN(b) = 1.556 (4) Å, and PN(c) = 1.572 (5) Å. This alternation in longer and shorter bonds has been detected for other partially alkyl- and aryl-substituted cyclophosphazenes[30-37] and has been ascribed to

(30) Mani, N. V.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1965**, *19*, 693.
(31) Mani, N. V.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1966**, *21*, 375.
(32) Ahmed, N. V.; Singh, P.; Barnes, W. H. *Acta Crystallogr., Sect. B* **1969**, *B25*, 316.
(33) Marsh, W. C.; Ranganathan, T. N.; Trotter, J.; Paddock, N. L. *Chem. Commun.* **1970**, 815.
(34) Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 569.

Table IV. Positional and Thermal Parameters and Their Standard Deviations for the Nonhydrogen Atoms of $N_3P_3Cl_5C_6H_5$ (5a)[a]

atom	x	y	z	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Cl(1)	0.2085 (2)	0.0041 (1)	0.3145 (1)	0.0605 (9)	0.084 (1)	0.0646 (9)	−0.0207 (9)	−0.0025 (8)	0.0207 (8)
Cl(2)	0.7989 (2)	0.1062 (1)	0.1736 (1)	0.0545 (8)	0.0723 (9)	0.0587 (7)	0.0084 (8)	0.0225 (6)	0.0102 (7)
Cl(3)	0.7507 (2)	−0.0297 (1)	0.3629 (1)	0.0657 (9)	0.0572 (8)	0.0688 (9)	0.0096 (8)	0.0005 (8)	0.0205 (7)
Cl(4)	0.5334 (2)	0.2018 (1)	0.5776 (1)	0.079 (1)	0.0621 (8)	0.0417 (7)	−0.0070 (8)	0.0119 (7)	−0.0028 (7)
Cl(5)	0.5490 (2)	0.3463 (1)	0.3885 (1)	0.090 (1)	0.0443 (8)	0.0590 (8)	−0.0033 (8)	0.0042 (8)	0.0011 (7)
P(1)	0.3317 (2)	0.10541 (10)	0.2527 (1)	0.0309 (7)	0.0461 (7)	0.0442 (7)	−0.0021 (7)	−0.0009 (6)	−0.0103 (7)
P(2)	0.6532 (2)	0.08214 (9)	0.2853 (1)	0.0321 (7)	0.0399 (7)	0.0397 (7)	0.0022 (6)	0.0024 (6)	−0.0039 (6)
P(3)	0.5236 (2)	0.21258 (9)	0.4081 (1)	0.0397 (7)	0.0426 (7)	0.0375 (7)	−0.0022 (7)	0.0011 (6)	−0.0108 (6)
N(1)	0.4860 (5)	0.0595 (3)	0.2192 (3)	0.033 (2)	0.048 (2)	0.053 (2)	0.004 (2)	−0.004 (2)	−0.021 (2)
N(2)	0.6720 (5)	0.1629 (3)	0.3750 (4)	0.032 (2)	0.057 (3)	0.054 (2)	−0.004 (2)	0.000 (2)	−0.023 (2)
N(3)	0.3560 (5)	0.1843 (3)	0.3465 (4)	0.034 (2)	0.070 (3)	0.061 (3)	0.005 (2)	0.003 (2)	−0.032 (2)
C(1)	0.2027 (5)	0.1435 (3)	0.1282 (4)	0.023 (2)	0.043 (3)	0.049 (3)	−0.002 (2)	0.002 (2)	−0.003 (2)
C(2)	0.1788 (7)	0.0910 (4)	0.0314 (5)	0.060 (3)	0.058 (3)	0.047 (3)	0.019 (3)	−0.009 (3)	−0.007 (3)
C(3)	0.0795 (8)	0.1212 (5)	−0.0647 (5)	0.073 (4)	0.078 (4)	0.055 (3)	0.018 (4)	−0.003 (3)	−0.009 (3)
C(4)	0.0054 (7)	0.2023 (5)	−0.0642 (5)	0.045 (3)	0.093 (4)	0.062 (3)	0.009 (3)	0.001 (3)	0.026 (3)
C(5)	0.0311 (7)	0.2567 (4)	0.0335 (5)	0.055 (3)	0.056 (3)	0.086 (4)	0.014 (3)	0.018 (3)	0.014 (3)
C(6)	0.1306 (6)	0.2275 (4)	0.1292 (5)	0.040 (3)	0.055 (3)	0.062 (3)	0.003 (3)	−0.001 (3)	−0.001 (3)

[a] The form of the isotropic thermal parameter is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

differences in the relative electronegativities of the pairs of substituents bound to each phosphorus atom bordering the P–N–P segment. This phenomenon will be discussed in the following section.

The unequal bond lengths within the phosphazene ring led to corresponding distortions in the endocyclic and exocyclic bond angles at P(1) (Figure 3 and Table V). Specifically, the N(1)–P(1)–N(3) angle ($\theta(1)$) is 117.3 (2)° and the Cl(1)–P(1)–C(1) angle ($\theta(5)$) is 103.5 (2)°. These results will also be discussed.

The P–Cl bonds at P(2) and P(3) are equal in length, with an average bond distance of 1.987 (3) Å. This value compares favorably to that observed for hexachlorocyclotriphosphazene.[38,39] The P(1)–Cl(1) bond (2.021 (2) Å) is lengthened considerably, presumably a consequence of electronic interactions that involve the geminal phenyl group. Because a phenyl group is more electron donating than a chlorine atom, the extra electron density serves to weaken and lengthen the geminal P–Cl bond. This type of P–Cl bond lengthening has been reported for other phosphazenes.[7,31]

The average Cl–P–Cl bond angle ($\theta(6)$) is 101.4 (8)° and is comparable to that reported for $(NPCl_2)_3$.[38,39] However, the individual angles Cl(2)–P(2)–Cl(3) (100.8 (1)°) and Cl(4)–P(3)–Cl(5) (101.9 (1)°) differ significantly. In addition, the average N···Cl distance (2.899 (10) Å) and Cl···Cl distance (3.074 (17) Å) are shorter than the sum of their van der Waals radii (3.3 and 3.60 Å, respectively). These attractions, together with crystal packing forces, could account for the difference in Cl–P–Cl angles. This effect has been detected for other phenyl-substituted cyclophosphazenes.[31]

The phenyl group is unexceptional, with an average C–C–C angle of 120.0 (4)° and an average C–C bond length of 1.369 (14) Å. The P(1)–C(1) distance is 1.778 (4) Å, which is similar to that reported for other phenyl-substituted cyclophosphazenes.[30-32]

Effect of Substituents of Phosphazene Rings. The incorporation of a tetracoordinate phosphorus atom into a cyclotriphosphazene ring results in a significant distortion of the bond angles away from the ideal tetrahedral geometry. Part of this distortion is a consequence of the constraints imposed by the six-membered ring, but substituent group effects are also important especially with respect to the exocyclic R–P–R bond angles. The structural parameters for a number of cyclotriphosphazenes are listed in Table V.

A "control" structure is clearly that of hexachlorocyclotriphosphazene, $(NPCl_2)_3$. Here, the ring bond angle at phosphorus is 118.4 (3)°, while the Cl–P–Cl exocyclic angle is 101.4 (2)°.[38,39] These deviations from ideal tetrahedral geometry probably reflect the constraints of the ring and a scissoring effect on the exocyclic angle.

As shown in the present work, the replacement of one chlorine atom in $(NPCl_2)_3$ by a phenyl group brings about a 1° narrowing of the N–P–N angle at that site, together with a 2° widening in the X–P–X exocyclic angle. Replacement of the unique chlorine atom in **5a** by phenyl decreases the ring bond angle at that phosphorus by a further 2°, while the X–P–X exocyclic angle is widened by an additional 1°. Similarly, when a methylene-*o*-

(35) Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 573.
(36) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Inorg. Chem.* **1980**, *19*, 2483.
(37) Allcock, H. R.; Scopelianos, A. G.; Whittle, R. R.; Tollefson, N. M. *J. Am. Chem. Soc.* **1983**, *105*, 1316.
(38) Bullen, G. J. *J. Chem. Soc. A* **1971**, 1450.
(39) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972; Chapter 3, Appendix I.

Table V. Comparison of Structural Data for $N_3P_3Cl_5C_6H_5$, 5a, and Related Phenyl- and Alkyl-Substituted Cyclophosphazanes[a]

bond length or angle	compound (reference)							
	$(NPCl_2)_3$ (38)	$N_3P_3Cl_5Ph$ (this work)	*gem*-$Ph_2N_3P_3Cl_4$ (30)	*gem*-$Ph_4N_3P_3Cl_4$ (31)	$N_3P_3Ph_6$ (32)	*gem*-*i*-Pr-H-$N_3P_3Cl_4$ (36)	*gem*-CH_3-CH_2-*o*-$C_2B_9H_{11}N_3P_3Cl_4$ (37)[b]
PN(a)	1.581 (3)	1.588 (2)	1.615 (5)	1.609 (8)	1.597 (6)	1.610 (6)	1.596 (2)
PN(b)		1.556 (4)	1.555 (5)	1.556 (9)		1.551 (6)	1.563 (3)
PN(c)		1.572 (5)	1.578 (5)	1.578 (8)		1.578 (6)	
N-P-N (θ(1))	118.4 (3)	117.3 (2)	115.2 (2)	115.5 (4)	117.8 (3)	115.6 (3)	114.6 (2)
P-N-P (θ(2))	121.4 (4)	121.6 (0)	122.0 (3)	121.0 (5)	121.1 (4)	122.1 (4)	
N-P-N (θ(3))		119.0 (3)	119.7 (3)	120.7 (5)		120.0 (3)	
P-N-P (θ(4))		120.9 (2)	119.2 (3)	124.9 (5)		119.4 (4)	
R-P-R (θ(5))		103.5 (2)	104.4 (3)	104.4 (5)	103.8 (3)	109 (3)	107.0 (2)
Cl-P-Cl (θ(6))	101.4 (2)	101.4 (8)	100.3 (1)	98.5 (2)		100.0 (1)	
dihedral angle[c]		46.8	51.8	54.4	57.5		

[a] Bond lengths (Å) and angles (deg) are mean values, with standard deviations from the average in parentheses. Refer to Figure 3 for the designation of the bonds and angles. [b] This compound has a proton bound to N(2); therefore only the listed data can be used for comparison. [c] Mean values of the dihedral angles between the weighted least-squares plane of the phosphazene and phenyl rings.

carboranyl group and a methyl group are present, the N–P–N angle at that site is 4° narrower than in $(NPCl_2)_3$ and the C–P–C angle is 6° wider. The most obvious explanation is that substituent group steric repulsions bring about a widening of the exocyclic angles, and the N–P–N angle becomes narrower to accommodate to the hybridization changes.

However, this does not explain the similar bond angle changes that occur when side groups less bulky than phenyl or alkylcarboranyl are present. For example, the presence of an isopropyl group and a hydrogen atom at the same phosphorus decreases the N–P–N angle by 3°, compared to $(NPCl_2)_3$.[36]

Undoubtedly, a contributing factor is the degree of electron supply into or electron withdrawal from the nearby P–N skeletal bonds by the substituent groups.[33-35] Electron supply into the bonds would lengthen them, distort the ring, and narrow the angle at that phosphorus, accordingly.

However, we believe that the geometry of the ring and the width of the X–P–X exocyclic angle is the end result of a subtle balancing of side group van der Waals repulsions and attractions, side group partial charge repulsions, and electronically induced changes in the skeletal bond lengths. At this time, it is not possible to gauge these influences separately.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, kindly supplied by Ethyl Corp. and the Firestone Tire and Rubber Co., was purified by fractional sublimation, followed by recrystallization from hexane. The Grignard reagents, methyllithium, $LiBEt_3H$ (1 M solution in THF), triethylborane (1 M solution in THF), and alkyl halides were commercial products obtained from Aldrich and were used as received. Tetrahydrofuran (THF) and acetonitrile were distilled into the reaction flask under an atmosphere of dry nitrogen from a sodium–benzophenone ketyl drying agent. Tetrachloromethane was distilled in a similar manner from phosphorus pentoxide. Tribromomethane (Aldrich) was used as received. Sodium fluoride (Mallinckrodt) was dried at 130 °C for 24 h before use. All reactions were performed under an atmosphere of dry nitrogen.

Preparation of 2. Compound **2** was prepared by a synthetic procedure reported previously.[1,3]

Synthesis of Phosphazene Anion 3. The bi(cyclophosphazene) **2** (5.0 g, 0.0071 mol) was stirred in THF (125 mL), and the solution was cooled to 0 °C. The reagent $LiBEt_3H$ (18 mL of a 1 M solution in THF) was added dropwise to the solution of **2** during 15 min. The reaction mixture was allowed to warm to room temperature and was stirred for 18 h. After this time, an analysis of the ^{31}P NMR spectrum of the reaction mixture indicated that compound **2** had been converted quantitatively to the triethylborane-substituted phosphazene anion **3**.

Synthesis of 4. A solution of **3** was prepared as described previously, and 2-propanol (5 mL) was added to destroy unreacted $LiBEt_3H$. The reaction solution was filtered through silica gel (proton-releasing agent), and the solvent was removed partially under reduced pressure until the total volume was approximately 25 mL. The resulting liquid residue was transferred to a vacuum sublimation apparatus and was absorbed on magnesium sulfate to prevent bumping during the sublimation. The sublimation apparatus was *quickly* evacuated, and the volatiles and residual solvent were removed during 4 h at $P = 0.05$ torr. [*Caution*: The removal of *all* solvent and adsorption of the residue on magnesium sulfate before transfer to the sublimation apparatus led on several occasions to the spontaneous inflammation of residual triethylborane. *Exercise extreme caution* when handling the crude residue, never evaporate the solvent to dryness, and evacuate the sublimation apparatus immediately after adsorption of the residue on magnesium sulfate.] The product **4** was then sublimed at 150 °C (0.05 torr) as white crystals. Cold water was not introduced into the cooling probe of the sublimation apparatus until the temperature was approximately 110 °C. Compound **4** was also

detected by ^{31}P NMR spectroscopy after treatment of a solution of **3** with CF_3COOH or CF_3CH_2OH. However, the compound undergoes rapid decomposition under these conditions and could not be isolated. Characterization data and yield are listed in Tables I and II.

Preparation of 5. Compounds **5** for which X = Cl and Br were prepared in a similar manner. The following is a typical procedure. Compound **4** (3.3 g, 9.3 mmol) was dissolved in CCl_4 (50 mL), and the solution was cooled to 0 °C. Excess chlorine (or 3 mL of bromine) was added to the solution, and the mixture was allowed to warm to room temperature over 18 h. After this time, the solvent was removed, and the crude product was purified by filtration of a solution in CH_2Cl_2 through neutral alumina. Following recrystallization from hexane, the products **5** were recovered as white crystals. For the preparation of **5**, where X = I, the procedure was modified as follows. To the solution of **4** in CCl_4, prepared as described previously, was added iodine (1.9 equiv), and the solution was stirred at 0 °C for 5.5 h. After this time, the solvent was removed under reduced pressure and residual iodine was separated by sublimation at room temperature. The crude product was purified by two recrystallizations from hexane to give **5** as white crystals. The compound discolored and decomposed at room temperature over several days during exposure to the atmosphere. Characterization data and yields are listed in Tables I and II.

Synthesis of 6. The following procedure is typical. A solution of **3** (14.2 mmol), prepared as described previously, was allowed to react with the appropriate alkyl halide (0.080 mol). When R was CH_3, the solution was stirred at 25 °C for 48 h, whereas the solution was heated to reflux temperature for 36 h for R = C_2H_5, n-C_3H_7, n-C_4H_9, and $CH_2CH{=}CH_2$ and for 72 h when R = i-C_3H_7. After this time, the solvent was removed under reduced pressure and the product was purified by filtration of a solution in CH_2Cl_2 through neutral alumina. Further purification by sublimation (125 °C (0.05 torr)) and recrystallization from hexane left the product as white crystals. Characterization data and yields are listed in Tables I and II.

Synthesis of 6 from 4. The following procedure is typical. Compound **4** (3.3 g, 9.3 mmol) was dissolved in THF (50 mL), and the solution was cooled to −75 °C. Methyllithium (5.2 mL of a 1.8 M solution in diethyl ether) was added dropwise over a period of 15 min. At no time was the temperature of the reaction mixture allowed to rise above −60 °C. When the addition was complete, the alkyl halide (0.080 mol) was added and the solution was allowed to warm to room temperature. The solvent was removed under reduced pressure, and the crude products were purified by filtration of a solution in CH_2Cl_2 through neutral alumina, followed by recrystallization from hexane to give product **6** as white crystals.

Synthesis of 3 from 4. Compound **4** (0.86 g, 2.44 mmol) and triethylborane (2.6 mL of a 1 M solution in THF) were stirred in THF (10 mL), and the solution was cooled to 0 °C. Methyllithium (1.6 mL of a 1.8 M solution in diethyl ether) was added dropwise to the mixture. When the addition was complete, an aliquot of the reaction mixture was withdrawn and the ^{31}P NMR spectrum was scanned. An analysis of the spectrum indicated that **4** had been converted quantitatively to **3**.

Reaction of 4 with $LiBEt_3H$. Compound **4** (1.9 g, 5.4 mmol) was dissolved in THF (50 mL), and the solution was cooled to 0 °C. The reagent $LiBEt_3H$ (8.9 mL of a 1 M solution in THF) was added dropwise over 30 min. After this time, the ^{31}P NMR spectrum of the reaction mixture was scanned. An analysis of the spectrum indicated that **4** had been converted quantitatively to **3**.

Reaction of 2 with Methyl Iodide in the Presence of Excess Triethylborane. Compound **2** (1.0 g, 1.42 mmol) was dissolved in a solution of triethylborane (50 mL of a 1 M solution in THF), and $LiBEt_3H$ (4.0 mL of a 1 M solution in THF) was added dropwise over 5 min to the solution at 0 °C. The solution was stirred for 24 h, and methyl iodide (0.016 mol) was added. After 48 h of stirring at 25 °C, an analysis of the ^{31}P NMR spectrum of the reaction mixture showed a 36% conversion to compound **6** (R = CH_3). (A 45° flip angle was employed in the Fourier transform data collection, and the pulse repetition rate was 30 s. The peak integration areas were accurate to less than ±3%.)

Preparation of 1,1-Diisopropyltetrachlorocyclotriphosphazene (8). A solution of 1-hydrido-1-isopropyltetrachlorocyclotriphosphazene (1.79 g, 5.61 mmol) in THF (125 mL) was prepared as reported previously[9] and was cooled to 0 °C. The reagent $LiBEt_3H$ (11.5 mL of a 1 M solution in THF) was added to give $N_3P_3Cl_4(i\text{-}C_3H_7)(^-BEt_3Li^+)$. After the mixture had been stirred for 24 h, the presence of the anion was confirmed by ^{31}P NMR spectroscopy. Resonances were observed at 90.0 [$P(i\text{-}C_3H_7)(^-BEt_3Li^+)$] and 3.9 ppm ($PCl_2$), and a PNP coupling constant of 66.3 Hz was recorded. Isopropyl iodide (4.0 mL, 0.040 mol) was added, and the solution was heated to reflux for 72 h. After this time, the solution was cooled to room temperature. An analysis of the ^{31}P NMR spectrum of the reaction mixture indicated that the anion was converted ≥90% to **8**. The solvent was removed under reduced pressure, and the product was purified by filtration of a solution in CH_2Cl_2 through neutral alumina, followed by sublimation at 140 °C (0.05 torr) onto a cold finger, cooled with a slush of dry ice and 2-propanol. At room temperature the product was a colorless oil. Characterization data are listed in Tables I and II.

Synthesis of 5a by the Reaction of 3 and CCl_4. A solution of **3** (14.2 mmol) was prepared as described previously. To this solution was added excess 2-propanol (2.0 mL), followed by excess CCl_4 (15.0 mL). (The 2-propanol was added to destroy any unreacted $LiBEt_3H$ and to capture the Cl_3C^- anion). The solution was stirred for 72 h. After this time, the solvent was removed under reduced pressure and the product was purified by filtration of a solution in CH_2Cl_2 through neutral alumina to give **5a** as a colorless oil. [Distillation of the product under reduced pressure (0.05 torr) was found to make recrystallization easier.] Recrystallization from hexane gave **5a** as colorless crystals.

Synthesis of 5b by the Reaction of 3 and CHBr. A solution of **3** (19.9 mmol) was prepared as described previously. To this solution was added excess 2-propanol (2.8 mL), followed by 0.97 equiv of $CHBr_3$ (1.75 mL, 96% purity). An analysis of the ^{31}P NMR spectrum of the reaction mixture indicated that the conversion of **3** to **5b** was complete within 15 min. The solvent was removed under reduced pressure, and the product was extracted from the residue with hexane (2 × 250 mL). The crude product was isolated as a white oil by removal of the hexane solvent under reduced pressure. The oil was purified by distillation under reduced pressure (0.05 torr), followed by recrystallization from pentane to give **5b** as colorless crystals.

Reaction of 3 with $(NPCl_2)_3$. A solution of **3** (8.52 mmol) was prepared as described previously. The solution was cooled to 0 °C, and a solution of $(NPCl_2)_3$ (2.96 g, 8.58 mmol) in THF (35 mL) was added dropwise. The mixture was stirred for 48 h. After this time, an analysis of the ^{31}P NMR spectrum of the reaction mixture indicated that **3** had been converted to **5a** and **2**. The solvent was removed under reduced pressure, and the crude products were purified by filtration of a solution in CH_2Cl_2 through neutral alumina. Extraction of the product mixture with hexane removed unreacted $(NPCl_2)_3$ and the product **5a** from the insoluble **2** (1.17 g, 39%). A ^{31}P NMR analysis of the mixture of $(NPCl_2)_3$ and **5a** indicated that the total yield of **5a** was 0.26 g (7.9% based on **3**). (A 45° flip angle was employed in the Fourier transform data collection, and the pulse repetition rate was 30 s. The peak integration areas were accurate to less than ±3%.)

Reaction of 5b with NaF. Compound **5b** (1.5 g, 3.48 mmol) and NaF (0.16 g, 3.81 mmol) were stirred in a degassed solution of acetonitrile (50 mL). The solution was heated to reflux for 48 h. After this time, the solution was cooled to room temperature and the solvent was removed under reduced pressure. The product was purified by filtration of a solution in CH_2Cl_2 through neutral alumina. The solvent was then removed under reduced pressure to give $N_3P_3Cl_4F(C_6H_5)$ (**5d**) as a colorless oil. Characterization data are listed in Tables I and II.

X-ray Structure Determination Technique. Crystals of $N_3P_3Cl_5C_6H_5$ (**5a**) suitable for X-ray diffraction examination were grown from pentane solution at −10 °C. A clear crystal, 0.26 × 0.28 × 0.32 mm, was mounted on a glass fiber, which was then transferred to a eucentric goniometer head and was attached to an Enraf-Nonius four-circle CAD4 automated diffractometer controlled by a PDP 8a computer. A full rotation orientation photograph was taken with a Polaroid cassette accessory, and 25 reflections of moderate intensity were chosen and accurately

centered with the use of the Enraf-Nonius program.[40] These reflections were then used to obtain an orientation matrix for data collection and suggested a monoclinic cell of dimensions a = 8.579 (1) Å, b = 14.612 (3) Å, c = 11.771 (3) Å, and β = 99.26 (1)° with V = 1456.4 (9) Å^3. The observed volume is consistent with that expected for Z = 4 and a d(calcd) = 1.775 g/cm^3. The observed systematic extinctions ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) uniquely defined the space group $P2_1/c$ (No. 14, C_{2h}^5).

A graphite single-crystal incident beam monochromator was used for data collection with Mo Kα radiation [λ(Mo Kα_1) = 0.710 73 Å] at room temperature (takeoff angle 2.80°). A θ–2θ scan method was used with a variable scan rate ranging from 5°/min for the most intense reflections to 1°/min for the weak ones. The angular scan width (ω) was variable and amounted to (1.0 + 0.347 tan θ)° both below Kα_1 and above Kα_2. Right and left backgrounds were each scanned for 25% of the total scan time. During data collection, three "standard" reflections were recorded after every 90 min of actual X-ray exposure time and were recentered automatically after every 250 reflections to monitor crystal stability and orientation. The standard reflections were used to rescale the data automatically to correct for drift during data collection (drift corrections were random and varied from 0.966 to 1.048). A total of 1916 reflections were collected for 3.0 $\leq 2\theta \leq$ 43.2°; of these 1614 had intensities with $I \geq 2\sigma(I)$ and were considered observed. No correction was made for absorption (μ = 12.95 cm^{-1} for Mo Kα).

The non-hydrogen atoms were located by direct methods using the program MULTAN78,[41] and their coordinates were determined by successive least-squares refinements. The hydrogen atoms were located and fixed at their calculated positions (C–H = 0.97 Å) and were assigned isotropic temperature parameters (B = 5.0 Å^2). Refinement of all anisotropic thermal parameters[42] of all non-hydrogen atoms and both hydrogen and non-hydrogen positional parameters using unit weights yielded a final R_1 = 0.035 and R_2 = 0.039. Here, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

In the final cycle, the maximum shift was 0.00 esd. Neutral atomic scattering factors[43] were used for all atoms and were corrected for anomalous dispersion[44] (both real and imaginary parts). The final difference map was essentially featureless with a maximum electron density of 0.15 e/Å^3 in the region of P(2).

Interatomic distances with esd's and positional and thermal parameters for the final cycle of refinement are listed in Tables III and IV, respectively. The following data are available as supplementary material: observed and calculated structure factor amplitudes (Table VI), selected weighted least-squares planes and distances of atoms from planes (Table VII), root-mean-square amplitudes of thermal vibration (Table VIII), and the stereoscopic view of the molecular structure (Figure 4).

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (Table VI), selected weighted least-squares planes and distances of atoms from planes (Table VII), and root-mean-square amplitudes of thermal vibration (Table VIII) and the stereoscopic view of the molecular structure (Figure 4) (11 pages). Ordering information is given on any current masthead page.

(40) All programs used in data collection, reduction, and refinement were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975, revised 1977.

(41) Main, P. "MULTAN78, A System of Computer Programs for the Automatic Solutions of Crystal Structures", Department of Physics, University of York: York, England, 1978; obtained from G. J. G. Williams, Brookhaven National Laboratories, Upton, N.Y.

(42) Isotropic thermal parameters are of the form $\exp[-B(\sin^2\theta)/\lambda^2]$. Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

(43) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(44) "International Tables for X-Ray Crystallography"; Knyoch Press: Birmingham, England, 1968; Vol. IV.

Functionally Substituted Derivatives of $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ (M = Cr, Mo, W) Complexes

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Compounds of the general type $(\eta^5\text{-}C_5H_4R)M(CO)_2NO$ have been prepared and their chemistry has been studied, where M = Cr, Mo, and W and R = CO_2CH_3, CHO, $COCH_3$, $C(CH_3)=CH_2$, and $CH[N(CH_3)_2]CH_3$. The carbomethoxy derivatives (R = CO_2CH_3) for all three metals (M = Cr, Mo, W) were obtained in yields of 12–79%. The acetyl (R = $COCH_3$) and formyl (R = CHO) derivatives were obtained only for M = Cr in yields of 79% and 56%, respectively. The isopropenyl organometallic monomers (R = $C(CH_3)=CH_2$) have been prepared for molybdenum and tungsten in good yields. Treatment of 6-(dimethylamino)fulvene with methyllithium followed by molybdenum hexacarbonyl and subsequent nitrosylation with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide gave the (dimethylamino)ethyl derivative (R = $CH[N(CH_3)_2]CH_3$; M = Mo) in 56% yield. A reaction between lithium nitrocyclopentadienide and chromium hexacarbonyl followed by acetic acid and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide gave the reduced compound $(\eta^5\text{-}C_5H_4NH_2)Cr(CO)_2NO$ in 7% yield.

Introduction

There is a small group of cyclopentadienylmetal compounds that exhibit aromatic-type reactivity. Included within this group are ferrocene, ruthenocene, osmocene, cymantrene and its technetium and rhenium analogues, (η^5-cyclopentadienyl)tetracarbonylvanadium, (η^5-cyclo-

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