# New Mono- and Trispirocyclotriphosphazenes from the Reactions of $(NPCl_2)_3$ with Aromatic Ortho Dinucleophiles

**Harry R. Allcock,* Ursula Diefenbach, and Shawn R. Pucher**

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

*Received February 19, 1993*®

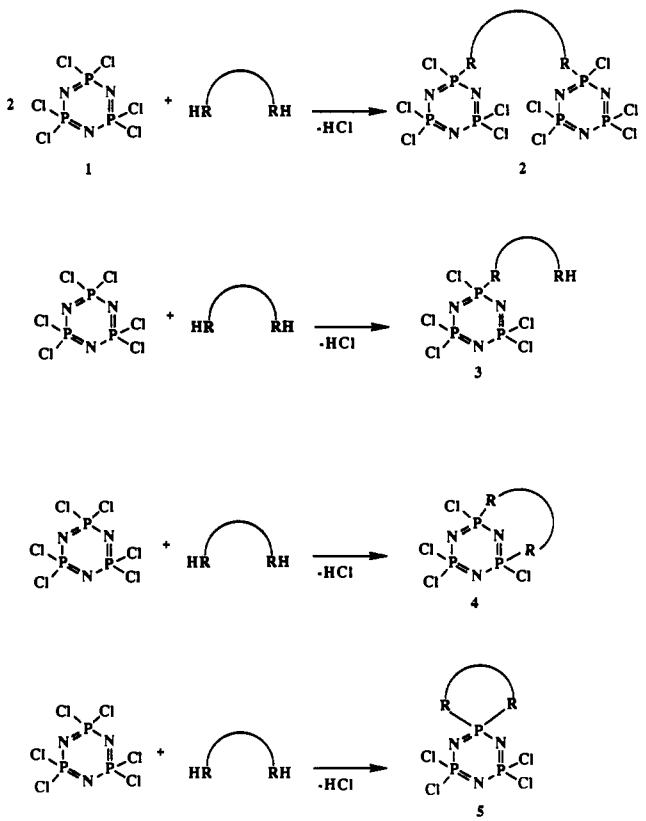
Hexachlorotriphosphazene reacted with 1,2-diaminobenzene, 1,2-diamino-4-methylbenzene, 1,2-diamino-4,5-dimethylbenzene, 1,2-diamino-4,5-dichlorobenzene, 2,3-diaminonaphthalene, 9,10-diaminophenanthrene, 2,3-diaminopyridine, trans 1,2-diaminocyclohexane, 1,2-diaminobenzophenone, and 1,2-benzenedithiol in THF in the presence of triethylamine to give the corresponding mono- or trispirocyclotriphosphazenes. The structures were examined by IR, $^{31}P$ NMR, and $^{1}H$ NMR spectroscopy, mass spectrometry, and elemental analysis.

## Introduction

The halogen replacement reactions of small-molecule cyclic chlorophosphazenes, $(NPCl_2)_x$, with monofunctional alkoxide ions or amines to give organophosphazenes, such as $[NP(OR)_2]_x$ or $[NP(NHR)_2]_x$, are well-known and fairly straightforward reactions.[1-4] However, hexachlorocyclotriphosphazene (**1**) reacts with difunctional reagents such as aliphatic or aromatic diols, diamines, or amino alcohols to yield five different types of products (Scheme 1). First, the dinucleophile may replace two chlorine atoms on different phosphazene rings to link these rings to give oligomers or polymers (**2**). Second, only one of the two functional groups may react with the cyclotriphosphazene to give products with pendent functional units (**3**). Third, both functional groups of the reagent may replace two chlorine atoms in a *cis* nongeminal arrangement to yield transannular substituted or *ansa* cyclotriphosphazenes (**4**). Fourth, *spiro* compounds (**5**) may form if the difunctional reagent reacts with two geminal chlorine atoms.[5-7,10-17] Finally, some aromatic ortho dinucleophiles cleave the phosphazene ring to generate ammonia and hexacoordinate or pentacoordinate organophosphorus molecules.[5-8]

The behavior of *aliphatic* difunctional reagents with cyclic phosphazene trimers has been studied in some detail. The reactions of aliphatic diols, such as 1,3-propanediol, with hexachlorocyclotriphosphazene yield mixtures of products based on **2–5**; however, the spiro arrangement (**5**) is favored.[18] Aliphatic diamines have also been shown to yield predominantly spiro-substituted cyclotriphosphazenes. Primary diamines usually react with hexachlorocyclotriphosphazene to give the corresponding monospiro derivatives,[19] although the formation of mixtures of mono-, di-, and trispiro-substituted cyclotriphosphazenes has been reported.[17] Secondary aliphatic diamines form mixtures of mono-, di-, and trispiro compounds.[20,21] Furthermore, aliphatic amino alcohols and inorganic difunctional nucleophiles, such as dihydrazido phosphoric acid derivatives favor the formation of the spirocyclic ring system.[14-17] Transannular and ring-linked compounds have been isolated in several reactions with aliphatic diamines, especially when the carbon chain between the two functional groups contains 8–10 atoms.[22-24]

**Scheme 1**




* Abstract published in *Advance ACS Abstracts*, June 1, 1994.

(1) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972; Chapters 6 and 7.
(2) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119.
(3) Krishnamurthy, S. S.; Sav, A. C. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 41.
(4) Shaw, R. A. *Z. Naturforsch.* **1976**, *31B*, 641.
(5) Allcock, H. R. *J. Am. Chem. Soc.* **1963**, *85*, 4050.
(6) Allcock, H. R. *J. Am. Chem. Soc.* **1964**, *86*, 2591.
(7) Allcock, H. R.; Kugel, L. *J. Am. Chem. Soc.* **1969**, *91*, 5452.
(8) Allcock, H. R.; Kugel, R. L.; Moore, G. Y. *Inorg. Chem.* **1975**, *14*, 2831.
(9) Bonnet, J. P.; Labarre, J.-F. *Inorg. Chim. Acta* **1988**, *149*, 187.
(10) Deutsch, W. F.; Guenduez, N.; Guenduez, T.; Hursthouse, H. B.; Shaw, C. S.; Shaw, R. A.; Tuezuen, M. *Phosphorus Sulfur* **1986**, *28*, 253.
(11) Willson, M.; Lafaille, L.; Videaud, L.; Labarre, J.-F. *Phosphorus Sulfur* **1987**, *29*, 147.
(12) Allcock, H. R.; Kugel, L. *Inorg. Chem.* **1966**, *5*, 1016.
(13) Allcock, H. R.; Turner, M. L.; Visscher, K. *Inorg. Chem.* **1992**, *31*, 4354.
(14) Engelhardt, U.; Diefenbach, U. *Z. Naturforsch.* **1990**, *44B*, 612.
(15) Engelhardt, U.; Diefenbach, U.; Damerius, R. *Z. Naturforsch.* **1990**, *45B*, 457.
(16) Diefenbach, U.; Engelhardt, U. *Z. Anorg. Allg. Chem.* **1992**, *609*, 67.
(17) Shaw, R. A. *Phosphorus Sulfur* **1989**, *45*, 103 and references therein.
(18) Alkubaisi, A. H.; Parkes, H. G.; Shaw, R. A. *Heterocycles* **1989**, *28* (1), 347.
(19) Krishnamurthy, S. S.; Ramachandran, K.; Vasudeva Murthy, A. R.; Shaw, R. A.; Woods, M. *J. Chem. Soc., Dalton Trans.* **1980**, 840.
(20) Chivers, T.; Hedgeland, R. *Can. J. Chem.* **1972**, *50*, 1017.
(21) de Ruiter, B.; Kuipers, G.; Bijlaart, J. H.; van de Grampel, J. C. *Z. Naturforsch.* **1982**, *37B*, 1425.
(22) Castera, P.; Faucher, J.-F.; Labarre, J.-F.; Perly, B. *J. Mol. Struct.* **1987**, *160*, 365.
(23) Guerch, G.; Labarre, J.-F.; Lahana, R.; Roques, R.; Sournies, F. *J. Mol. Struct.* **1983**, *99*, 275.
(24) Castera, P.; Faucher, J.-F.; Guerch, G.; Lahana, R.; Mahmoun, A.; Sournies, F.; Labarre, J.-F. *Inorg. Chim. Acta* **1985**, *108*, 29.

0020-1669/94/1333-3091$04.50/0 

The situation with *aromatic* difunctional reagents is more complicated. We described previously the synthesis of mono-, di-, and trispiro-substituted cyclotriphosphazenes by allowing hexachlorocyclotriphosphazene to react with aromatic dinucleophiles.[5-8,12,25-27] In that earlier work, the reactivity of aromatic diols such as catechol or 2,3-naphthalenediol was studied in detail. The formation of *ansa* derivatives from aromatic diols and diamines was reported by us recently.[13] A surprising observation was that, for one particular difunctional molecule, catechol, the quantity of the dinucleophile employed in the reaction does not influence the nature of the product. For example, catechol reacts with hexachlorocyclotriphosphazene to give the stable trispiro-substituted ring system regardless of the quantity of catechol used. In a side reaction in the presence of triethylamine, catechol induces the decomposition of the phosphazene ring and the formation of the phosphate anion, $[P(O_2C_6H_5)_3]^-$.[25] Similarly $\sigma$-aminophenol causes the degradation of the phosphazene system, but in this case, spiro phosphazenes were not detected.[7,12] Although reactions with aromatic diamines have been reported in the past,[12,13] no systematic investigation had been carried out.

Recent work in our laboratory has shown that aromatic spiro phosphazenes have some interesting properties. For example, ring opening polymerization to yield polyphosphazenes, or ring expansion to higher cyclic species, can occur when mono- or trispiroaryloxy compounds are heated to temperatures above 250 °C.[28] A reason for the interest in these ring expansion/polymerization reactions is that they offer the prospect of direct conversion of a cyclic phosphazene to a polymer without the need for macromolecular substitution reactions.[29,30]

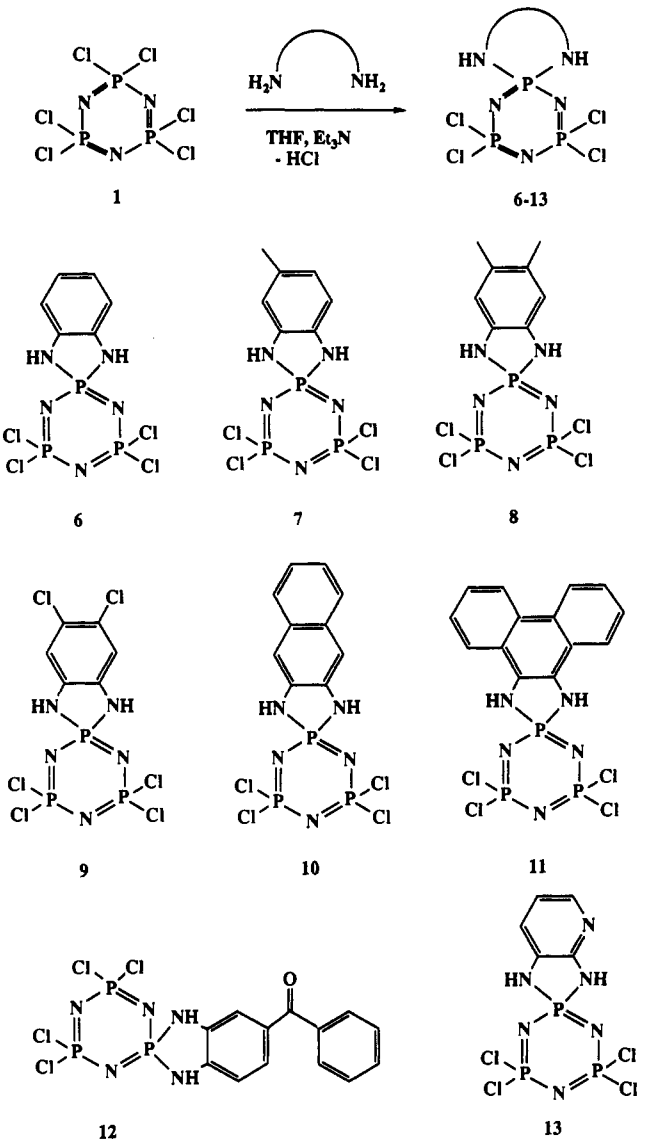
Previously, we also showed that trispirophosphazenes with aromatic dioxy units form crystalline inclusion adducts in the solid state when they are brought into contact with a wide variety of organic liquids and vapors.[31] The organic guest molecules occupy tunnels that are formed within the crystal lattice during the inclusion process.[17,26,31-33] Several organic monomers, such as styrenes, acrylonitrile, and butadiene, undergo stereocontrolled polymerization within the phosphazene host system after exposure to $\gamma$ radiation.[34] The only diaminospirocyclotriphosphazene that has been investigated for its clathration properties is tris(benzene-1,2-diamino)cyclotriphosphazene (**14**).[31] This compound forms inclusion adducts with ketones by a mechanism that apparently involves hydrogen bonding rather than via the van der Waals interactions that stabilize the arylenedioxy clathrates.[31]

With these facts in mind we have undertaken the synthesis of a range of new (arylamino)spirophosphazenes, shown as **6–20** in Schemes 2 and 3, and one (arylthio)spirophosphazene (**17**). The objective was to explore the limits of the side group cyclization process with respect to variations in (a) the use of diamino or dithiol reactive units (as distinct from arylenedioxy units) and (b) changes in the struture of the aromatic units and substituents linked to those rings.

## Results and Discussion

**General Strategy.** The compounds shown as **6–21** reflect a number of structural features that are of long range interest from the viewpoints of clathration, substitution mechanisms, and phosphazene ring-opening polymerization. First, all except one possess NH units that link the organic side groups to the phosphazene ring. These units are, in principle, capable of hydrogen bonding to nearby phosphazene molecules in a crystalline lattice and to potential guest molecules such as ketones, esters, etc. The sulfur-linked molecule, **17**, represents a type of structure that is quite rare in phosphazene chemistry. Second, a wide variation was explored in the organic side groups, from simple aryl units as in **6–8**, **4**, **15**, and **17** to halogenated (**9**, **16**), polyaromatic (**10–12**, **19**, **20**), heterocyclic (**13**), and alicyclic (**18**, **21**) units. These variations constitute a prelude to probing the relationship of side group structure to clathration, polymerization, and the spirocyclization process. Third, some of the molecules (**6–13**) have only one spiro structure per phosphazene ring, with the remaining side units being unreacted chlorine atoms. These compounds are potentially useful as intermediates for further halogen replacement reactions and as possible monomers for ring-opening polymerization studies. The trispiro molecules, **14–18**, are prospective clathration hosts and possible monomers for ring-opening polymerization. And finally, compound **21** is an interesting species for studies of the mechanism of spirocyclization and as a reaction intermediate for the formation of cyclomatrix polymers.

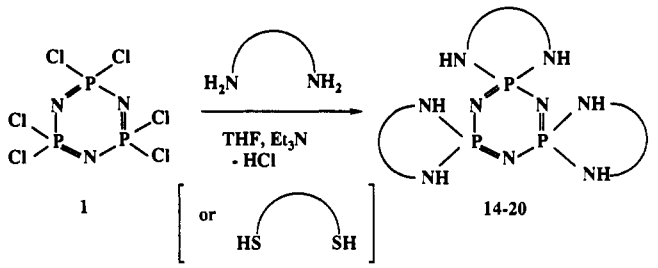
**Scheme 2**

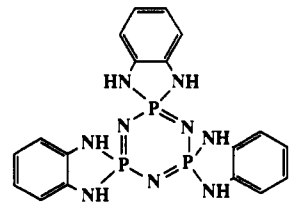


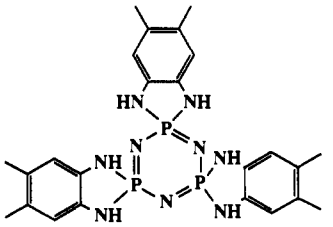

**Preparation of Monospiro Compounds 6–13.** The general reaction route to obtain compounds **6–13** is shown in Scheme 2.

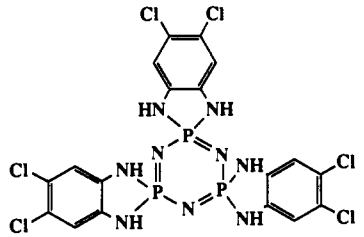
(25) Allcock, H. R.; Walsh, E. J. *Inorg. Chem.* **1971**, *10*, 1643.
(26) Allcock, H. R.; Allen, R. W.; Bissell, E. C.; Smeltz, L. A.; Teeter, M. *J. Am. Chem. Soc.* **1976**, *98*, 5120.
(27) Allcock, H. R.; Kugel, R. L. *J. Chem. Soc., Chem. Commun.* **1968**, *24*, 1606.
(28) Allcock, H. R.; Turner, M. L. *Macromolecules* **1993**, *26*, 3.
(29) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.
(30) Allcock, H. R.; Patterson, D. B. *Inorg. Chem.* **1977**, *16*, 197.
(31) Allcock, H. R. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, Chapter 8.
(32) Allcock, H. R.; Siegel, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 5140.
(33) Allcock, H. R.; Ferrar, W. T.; Levin, M. L. *Macromolecules* **1982**, *15*, 697.
(34) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1990; Chapter 8.

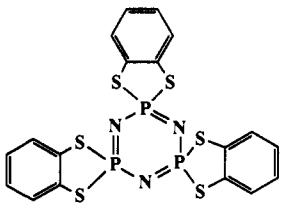
**Scheme 3**

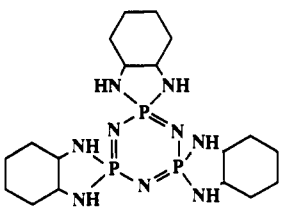


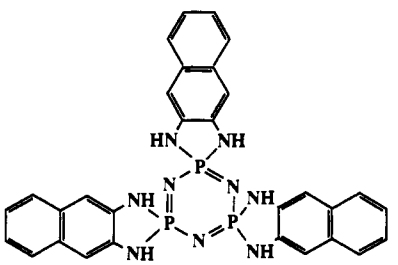



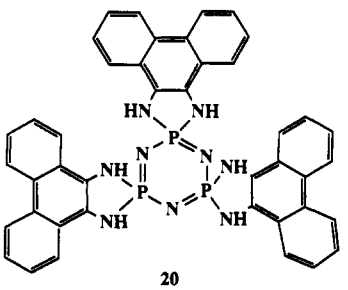



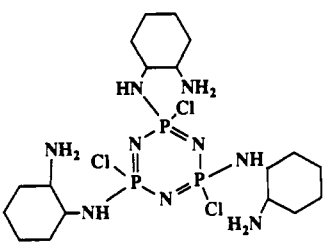

Thus, the monospiro compounds were prepared by the reactions of hexachlorocyclotriphosphazene (**1**) with the appropriate dinucleophiles in THF solution in the presence of triethylamine as a hydrochloride acceptor. A geminal attack by primary amino groups is known to be favored in this medium.[35-37] To avoid side reactions, a dilute solution of the difunctional reagent was added slowly and dropwise to a dilute solution of hexachlorocyclotriphosphazene (**1**).

The reactivity of the diamine decreased noticeably as the size of the organic group increased. The reaction of 1,2-diaminobenzene with hexachlorocyclotriphosphazene (**1**) yielded the monospiro-substituted compound (**6**) in 3–5 h at room temperature in a clean reaction.[12] However, the bulkier diaminotoluene and diamino-*o*-xylene required 48 h to complete the substitutions. 2,3-Diaminonaphthalene, 9,10-diaminophenanthrene, and 1,2-diaminobenzophenone required 200 h in refluxing THF before the formation of the corresponding monospiro derivatives (**10–12**) could be detected by $^{31}P$ NMR spectroscopy. The yields of species **10–12** were quite low (7–12%), and this reflects the low reactivity of the bulky aromatic amines and their tendency to generate mixtures of difficult-to-identify side products. The structures of the monospiro compounds **6–13** were monitored by IR, $^{1}H$ NMR, and $^{31}P$ NMR spectroscopy, mass spectrometry, and elemental analysis. Table 1 shows the characterization data for compounds **6–13**.

In contrast to the above reactions, *trans*-1,2-diaminocyclohexane reacted with **1** exclusively to give the stable trispiro analogue (**18**). The monospiro-substituted product could not be detected by $^{31}P$ NMR spectroscopy at any stage during the reaction.

**Preparation of Trispiro Compounds 14–20.** The reaction route used to synthesize the trispiro derivatives **14–20** (Scheme 3) was similar to the one described above for the preparation of the monospiro compounds **6–13**. The ratios of the dinucleophiles to hexachlorocyclotriphosphazene were >3:1 to force the system to complete substitution. For the same reason, high concentrations of the reactants and higher reaction temperatures were used to increase the speed of the reactions. The symmetrically substituted dinucleophiles 1,2-benzenedithiol, 1,2-diaminobenzene, 1,2-diamino-4,5-dimethylbenzene, 1,2-diamino-4,5-dichlorobenzene, 2,3-diaminonaphthalene and 9,10-diaminophenanthrene yielded trispiro compounds **14–17**, **19**, and **20**. Characterization data for compounds **14–20** are shown in Table 2.

**Behavior with 1,2-Diaminocyclohexane.** *cis*- and *trans*-1,2-diaminocyclohexane were allowed to react with hexachlorocyclotriphosphazene (**1**) in the same manner as in the other reactions. The *trans* derivative yielded tris(cyclohexane-1,2-diamino)cyclotriphosphazene (**18**). By contrast, ring closure did not occur when **1** was allowed to interact with *cis*-1,2-diaminocyclohexane. The formation of a trisubstituted "pendent" product, **21**, was detected by $^{31}P$ NMR spectroscopy and mass spectrometry. It




21

seems likely that a geminal attack at phosphorus is not possible for the *cis*-reagent because the diamino groups are more widely separated in the *cis* than in the *trans* isomer. Thus, in a chair conformation of the cyclohexane ring, both amino groups of the

(35) Gabay, Z.; Goldschmidt, J. M. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1457.
(36) Goldschmidt, J. M. E.; Licht, E. *J. Chem. Soc., Dalton Trans.* **1972**, 732.
(37) Lehmann, H.-A. *Pure Appl. Chem.* **1975**, *44*, 221.

**Table 1.** Characterization Data for Compounds **6–13**

| compds | $^{31}$P NMR,[a] ppm | $^{1}$H NMR,[a] ppm | IR | mass spectrometry | mp, °C | elemental anal. | % C | % H | % N |
|---|---|---|---|---|---|---|---|---|---|
| **6** | 21.3 (2P, d) | 7.4 (2H, d) | 3345 (NH) | calcd 383 | >310 | calc | 18.80 | 1.57 | 18.23 |
| | 13.6 (1P, t) | 6.9 (4H, m) | 1250–1200 (P═N) | found 383 | | found | 18.89 | 1.38 | 18.15 |
| | $J_{PNP}$ = 70 Hz | $J_{PH}$ = 11 Hz | 568, 512 (PCl) | | | | | | |
| **7** | 21.5 (2P, d) | 7.6 (2H, d) | 3250 (NH) | calcd 397 | 247–249 | calcd | 21.15 | 2.01 | 17.62 |
| | 13.5 (1P, t) | 6.8 (3H, m) | 1220–1180 (P═N) | found 398 | | found | 21.39 | 1.89 | 17.90 |
| | $J_{PNP}$ = 67 Hz | 2.2 (3H, s) | 583, 522 (PCl) | | | | | | |
| | | $J_{PH}$ = 15 Hz | | | | | | | |
| **8** | 18.9 (2P, d) | 7.2 (2H, d) | 3352 (NH) | calcd 411 | 259–262 | calcd | 23.36 | 2.43 | 17.08 |
| | 13.5 (1P, t) | 6.7 (2H, s) | 1290–1200 (P═N) | found 411 | | found | 23.62 | 2.61 | 16.87 |
| | $J_{PNP}$ = 63 Hz | 2.2 (6H, s) | 577, 520 (PCl) | | | | | | |
| | | $J_{PH}$ = 13 Hz | | | | | | | |
| **9** | 21.6 (2P, d) | 7.3 (2H, d) | 3482 (NH) | calcd 452 | 273–277 | calcd | 15.93 | 0.88 | 15.49 |
| | 11.6 (1P, t) | 6.9 (2H, s) | 1230–1200 (P═N) | found 453 | | found | 16.27 | 0.92 | 15.28 |
| | $J_{PNP}$ = 60 Hz | $J_{PH}$ = 17 Hz | 571, 514 (PCl) | | | | | | |
| **10** | 20.6 (2P, d) | 8.4 (2H, d) | 3363 (NH) | calcd 433 | >310 | calcd | 27.15 | 1.97 | 15.84 |
| | 15.0 (1P, t) | 7.7–6.9 (6H, m) | 1320–1197 (P═N) | found 433 | | found | 27.74 | 1.86 | 16.13 |
| | $J_{PNP}$ = 55 Hz | $J_{PH}$ = 16 Hz | 578, 517 (PCl) | | | | | | |
| **11** | 21.4 (2P, d) | 8.1–7.1 (8H, m) | 3200 (NH) | calcd 483 | 280–290 | calcd | 34.54 | 2.07 | 13.56 |
| | 16.9 (1P, t) | 6.5 (2H, d) | 1260–1160 (P═N) | found 483 | | found | 34.81 | 2.09 | 14.50 |
| | $J_{PNP}$ = 51 Hz | $J_{PH}$ = 14 Hz | 580, 520 (PCl) | | | | | | |
| **12** | 20.4 (2P, d) | 7.7 (2H, d) | 3226 (NH) | calcd 487 | 279–284 | calcd | 32.03 | 2.05 | 14.37 |
| | 13.6 (1P, t) | 7.8–7.2 (7H, m) | 1690 (C═O) | found 488 | | found | 31.89 | 2.12 | 14.69 |
| | $J_{PNP}$ = 63 Hz | 6.8 (1H, d) | 1210–1200 (P═N) | | | | | | |
| | | $J_{PH}$ = 14 Hz | 576, 514 (PCl) | | | | | | |
| **13** | 21.2 (2P, d) | 7.6 (2H, d) | 3314 (NH) | calcd 384 | 242–244 | calcd | 15.63 | 1.30 | 21.86 |
| | 15.0 (1P, t) | 7.2 (3H, m) | 1245–1230 (P═N) | found 384 | | found | 16.12 | 1.44 | 22.78 |
| | $J_{PNP}$ = 69 Hz | $J_{PH}$ = 14 Hz | 572, 524 (PCl) | | | | | | |

[a] Spectra for compounds **6–9** and **11–13** were run in $CDCl_3$, and spectra of compound **10** were run in THF-$d_8$.

**Table 2.** Characterization Data for Compounds **14–20**

| compds | $^{31}$P NMR[a], ppm | $^{1}$H NMR,[a] ppm | IR | mass spectrometry | mp, °C | elemental anal. | % C | % H | % N |
|---|---|---|---|---|---|---|---|---|---|
| **14** | 21.3 | 8.1 (2H, br) | 3200 (NH) | calcd 453 | >310 | calcd | 47.68 | 3.97 | 27.81 |
| | | 6.8 (4H, m) | 1270–1190 (P═N) | found 453 | | found | 48.03 | 3.90 | 28.00 |
| **15** | 21.6 | 8.2 (2H, br) | 3170 (NH) | calcd 537 | >310 | calcd | 53.63 | 5.59 | 23.42 |
| | | 6.6 (2H, s) | 1290–1210 (P═N) | found 538 | | found | 54.00 | 5.70 | 23.26 |
| | | 2.2 (6H, s) | | | | | | | |
| **16** | 20.4 | 8.3 (2H, br) | 3363 (NH) | calcd 660 | >310 | calcd | 32.73 | 1.82 | 19.09 |
| | | 6.8 (2H, s) | 1240–1220 (P═N) | found 661 | | found | 33.12 | 1.88 | 18.79 |
| **17** | 54.6 | 7.4 (4H, m) | 2635 (Ar–S) | calcd 555 | 265–268 | calcd | 38.92 | 2.16 | 7.57 |
| | | | 1260–1200 (P═N) | found 555 | | found | 38.74 | 2.39 | 7.63 |
| **18** | 24.6 | 8.2 (2H, br) | 3128 (NH) | calcd 471 | 234–239 | calcd | 45.86 | 6.37 | 26.75 |
| | | 2.3 (2H, td) | 1250–1220 (P═N) | found 471 | | found | 46.04 | 6.23 | 26.82 |
| | | 1.7–0.9 (8H, m) | | | | | | | |
| **19** | 19.5 | 8.3 (2H, br) | 3250 (NH) | calcd 604 | >310 | calcd[b] | 53.34 | 4.77 | 18.66 |
| | | 7.8–6.8 (8H, m) | 1250–1140 (P═N) | found 604 | | found | 53.82 | 4.51 | 17.45 |
| **20** | 22.9 | 8.4 (2H, br) | 3190 (NH) | calcd 754 | >310 | calcd[b] | 63.88 | 4.34 | 15.96 |
| | | 8.9–7.4 (8H, 2d, 2t) | 1280–1160 (P═N) | found 754 | | found | 63.83 | 5.14 | 15.29 |

[a] Spectra of compounds **14–16** and **18–20** were obtained in DMSO-$d_6$. Spectra of compound **17** were obtained in THF-$d_8$. [b] Elemental analyses of compounds **19** and **20** were calculated for the presence of traces of water that could not be removed.

*trans* derivative are positioned either axial or equatorial. The diequatorial conformation probably provides an ideal distance for ring closure because of the similarity to the distance in the planar aromatic dinucleophiles. By contrast, one of the amino groups of the *cis* isomer is always placed in an axial position and the other in an equatorial position. This arrangement is obviously unfavorable for the formation of the spirocyclic ring system.

The behavior of these compounds in polymerization reactions and in clathration is still under investigation. However, preliminary results indicate that some of these compounds participate in ring-expansion reactions when heated, and this will be the subject of a future paper.

## Experimental Section

**Materials.** Hexachlorocyclotriphosphazene was provided by Ethyl Corp. It was recrystallized from hexane and sublimed (30 °C, 0.05 mmHg) before use. 1,2-Diaminobenzene, 1,2-diamino-4-methylbenzene, 1,2-diamino-4,5-dimethylbenzene, 1,2-diamino-4,5-dichlorobenzene, 2,3-diaminopyridine, *cis*- and *trans*-1,2-diaminocyclohexane, 2,3-diaminonaphthalene, 9,10-diaminophenanthrene, 1,2-diaminobenzophenone, and 1,2-benzenedithiol (Aldrich) were used as received. THF was distilled from sodium benzophenone ketal under dry argon. Hexane and methylene chloride were distilled from calcium hydride. All manipulations were performed under dry argon using standard Schlenk techniques.

**Equipment.** $^{31}$P (145 MHz), $^{13}$C (90 MHz), and $^{1}$H (360 MHz) NMR spectra were obtained by use of a Bruker WM 360 spectrometer. Low-field $^{31}$P NMR (36.2 MHz) spectra were recorded using a JEOL FX 90Q NMR spectrometer. $^{31}$P NMR shifts were referenced to external $H_3PO_4$ with positive shifts recorded downfield from the reference. $^{1}$H NMR spectra were referenced to external tetramethylsilane. A Perkin-Elmer infrared Fourier transform spectrometer was used to obtain IR spectra. Samples were used as KBr pellets. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

**Synthesis of $N_3P_3Cl_4[(NH)_2C_6H_4]$ (6).** This compound was prepared by a route similar to one described previously[12] from hexachlorocyclotriphosphazene (**1**) (5.0 g, 0.0144 mol) in THF (200 mL), 1,2-diaminobenzene (1.55 g, 0.014 mol), and triethylamine (10 mL, 0.035 mol) in THF (100 mL) at 25 °C. After 5 h, the $^{31}$P NMR spectrum showed that the desired product **6** was formed quantitatively. The reaction

mixture was filtered and the solvent removed to afford a beige solid. The crude product was then placed in a Soxhlet extraction apparatus, and the solids were extracted with hexane for 120 h. After the hexane was cooled, compound **6** crystallized from solution. Recrystallization from hexane yielded 3.6 g (66%) of pure compound **6**.

**Synthesis of $N_3P_3Cl_4[(NH)_2C_6H_3(CH_3)]$ (7).** Hexachlorocyclotriphosphazene (**1**) (2.5 g, 0.0072 mol) was dissolved in THF (100 mL). A solution of 1,2-diamino-4-methylbenzene (0.88 g, 0.0072 mol) and triethylamine (2.1 mL, 0.0144 mol) in 100 mL THF was added dropwise at room temperature. After the mixture was stirred for 48 h, the monospiro product **7** was formed quantitatively. The reaction mixture was filtered, and the solvent was removed under reduced pressure. The crude product was placed in a Soxhlet extractor and extracted with hexane for 144 h. After the hexane was cooled, compound **7** crystallized from solution. Recrystallization from hexane yielded the product as colorless crystals (1.4 g, 48%).

**Synthesis of $N_3P_3Cl_4[(NH)_2C_6H_2(CH_3)_2]$ (8).** A solution of 1,2-diamino-4,5-dimethylbenzene (1.96 g, 0.0144 mol) and triethylamine (4 mL, 0.0288 mol) in THF (100 mL) was added slowly to a solution of hexachlorocyclotriphosphazene (5.0 g, 0.0144 mol) in THF. The mixture was stirred for 48 h at room temperature. The reaction mixture was filtered, and the solvent was removed. Soxhlet extraction with hexane for 120 h and recrystallization from hexane yielded **8** as a beige crystalline solid (2.4 g, 41%).

**Synthesis of $N_3P_3Cl_4[(NH)_2C_6H_2Cl_2]$ (9).** A solution of 1,2-diamino-4,5-dichlorobenzene (2.55 g, 0.0144 mol) and triethylamine (4 mL, 0.0288 mol) in THF (100 mL) was added slowly to a solution of hexachlorocyclotriphosphazene (5.0 g, 0.0144 mol). The reaction mixture was stirred for 72 h at room temperature. The mixture was filtered and the solvent removed to yield a beige solid. The crude product was purified by column chromatography with silica gel using THF/hexane (1:1) as the eluent. This procedure gave pure product **9** (2.6 g, 40%).

**Synthesis of $N_3P_3Cl_4[(NH)_2C_{10}H_6]$ (10).** Hexachlorocyclotriphosphazene (**1**) (3.5 g, 0.01 mol) and triethylamine (3 mL, 0.02 mol) were dissolved in THF (200 mL). A solution of 2,3-diaminonaphthalene (1.6 g, 0.01 mol) in THF (150 mL) was added dropwise over a period of 1 h. The mixture was heated to reflux for 1 week. The white precipitate (triethylamine hydrochloride) was removed by filtration through a glass frit. The solvent and unreacted base were removed under reduced pressure. To separate **10** from side products and unreacted starting material, the mixture was first dissolved in THF, and hexane was added to precipitate the impurities. The mixture was cooled to −10 °C and filtered, and more hexane was added. This procedure was repeated four times. The last of the fractions obtained contained the product, which was recrystallized from THF/hexane to yield the white crystalline compound **10** (0.5 g, 11.5%).

**Synthesis of $N_3P_3Cl_4[(NH)_2C_{14}H_8]$ (11).** 9,10-Diaminophenanthrene (2.08 g, 0.01 mol) was dissolved in THF (200 mL). The solution was added dropwise to a stirred solution of hexachlorocyclotriphosphazene (3.5 g, 0.01 mol) and triethylamine (3 mL, 0.02 mol) in THF (300 mL). The mixture was heated to reflux for 1 week. The triethylamine hydrochloride was filtered off, and the solvent and unreacted base were removed under reduced pressure. The crude product mixture was then dried under vacuum. Extraction with *n*-hexane in a Soxhlet extractor yielded **11** as a pale, green solid. After recrystallization from THF/hexane, pure compound **11** was obtained (0.3 g, 6.2%).

**Synthesis of $N_3P_3Cl_4[(NH)_2C_{13}H_8O]$ (12).** Hexachlorocyclotriphosphazene (**1** (2.5 g, 0.0072 mol) was dissolved in THF (100 mL). To the solution of **1** was added 1,2-diaminobenzophenone (1.53 g, 0.0072 mol) and triethylamine (2 mL, 0.01436 mol) in THF (100 mL). The reaction mixture was maintained at 50 °C for 96 h. The reaction mixture was filtered and the solvent removed to yield a beige solid. This crude product **12** was initially purified by Soxhlet extraction with hexane to yield a white solid. The product was further purified by recrystallization from THF to afford pure compound **12** as a white solid (0.23 g, 6.8%).

**Synthesis of $N_3P_3Cl_4[(NH)_2C_5H_5N]$ (13).** Hexachlorocyclotriphosphazene (1.0 g, 0.0029 mol) was dissolved in THF (50 mL). 2,3-Diaminopyridine (0.4 mL, 0.0029 mol) and triethylamine (3 mL, 0.01 mol) were dissolved in THF (25 mL) and added slowly to the solution of compound **1**. The reaction proceeded at room temperature for 48 h. The reaction mixture was filtered and the solvent removed to give a brown solid. This crude product was then purified by Soxhlet extraction with hexane for 168 h to give compound **13** as a beige solid. Product **13** was further purified by recrystallization from hexane (0.24 g, 23%).

**Synthesis of $N_3P_3[(NH)_2C_6H_4]_3$ (14).** This compound was prepared by a variation of a method described previously[6] from 1,2-diaminobenzene (4.8 g, 0.044 mol), hexachlorocyclotriphosphazene (**1**) (5.0 g, 0.0144 mol), and triethylamine (12.3 mL, 0.088 mol) in THF (300 mL) at 45 °C. After 48 h, the $^{31}P$ NMR spectrum of the reaction mixture indicated that the reaction had gone to completion. The reaction mixture was then cooled and filtered through a fritted funnel. The solids were washed with THF (200 mL) and with water (200 mL). The crude product **14** was dried under vacuum. The solids were recrystallized from hot *o*-xylene (125 mL). Compound **14** was obtained as yellow needlelike crystals (3.7 g, 56%).

**Synthesis of $N_3P_3[(NH)_2C_6H_2(CH_3)_2]_3$ (15).** Hexachlorocyclotriphosphazene (**1**) (5.0 g, 0.0144 mol) dissolved in THF (200 mL) was allowed to react with a solution of 1,2-diamino-4,5-dimethylbenzene (5.9 g, 0.044 mol) in the presence of triethylamine (12.3 mL, 0.088 mol). The reaction temperature was raised to approximately 66 °C. After 60 h, the reaction was complete as determined by $^{31}P$ NMR spectroscopy. The reaction mixture was filtered through a fritted funnel and washed with THF (200 mL) and water (200 mL). The crude product was recrystallized from hot *o*-xylene to obtain **15** as beige crystals (3.4 g, 44%).

**Synthesis of $N_3P_3[(NH)_2C_6H_2Cl_2]_3$ (16).** Hexachlorocyclotriphosphazene (**1**) (5.0 g, 0.0144 mol) dissolved in THF (200 mL) was treated with a solution of 1,2-diamino-4,5-dichlorobenzene (7.8 g, 0.044 mol) in the presence of triethylamine (12.3 mL, 0.088 mol). The reaction temperature was raised to approximately 66 °C. After 96 h, the reaction was complete as determined by $^{31}P$ NMR spectroscopy. The reaction mixture was filtered through a fritted funnel and then washed with THF (200 mL) and water (200 mL). The crude product was recrystallized from hot *o*-xylene and benzene to obtain **16** as a beige solid (2.5 g, 30%).

**Synthesis of $N_3P_3[S_2C_6H_4]_3$ (17).** A solution of 1,2-benzenedithiol (1.3 g, 0.0092 mol) in THF (100 mL) was added dropwise to a stirred solution of hexachlorocyclotriphosphazene (**1**) (1.07 g, 0.0031 mol). Triethylamine (3 mL, 0.0184 mol) in THF (200 mL) was then added slowly. The reaction mixture was warmed to 40 °C for 96 h. After being cooled to room temperature, the reaction mixture was filtered, the filtrate collected, the solvent removed, and the crude product washed with water (400 mL). Crude product **17** was dried under vacuum. Recrystallization from hot *o*-xylene afforded **17** as a yellow solid (0.33 g, 19.2%).

**Synthesis of $N_3P_3[(NH)_2C_6H_{10}]_3$ (18).** *trans*-1,2-diaminocyclohexane (12.8 mL, 0.0259 mol) was dissolved in THF (150 mL) and was added dropwise to a stirred solution of hexachlorocyclotriphosphazene (3.0 g, 0.0086 mol) in THF (100 mL). After the addition of the diamine to the solution of **1**, triethylamine (7.26 mL, 0.0518 mol) was then added via syringe. After this was stirred for 48 h at room temperature, the $^{31}P$ NMR spectrum of the reaction mixture showed that **18** had formed quantitatively. The reaction mixture was filtered through a fritted funnel. The filtrate was collected and the solvent removed to yield a yellow solid. Crude product **18** was then washed with water (600 mL) and dried under vacuum. Recrystallization from hot *o*-xylene yielded **18** as a yellow solid (1.24 g, 31%).

**Synthesis of $N_3P_3[(NH)_2C_{10}H_6]_3$ (19).** Hexachlorocyclotriphosphazene (**1**) (2.0 g, 0.0058 mol) and triethylamine (10 mL, 0.07 mol) were dissolved in 100 mL of THF. A solution of 2,3-diaminonaphthalene (3.8 g, 0.024 mol) in 100 mL of THF was added dropwise to the stirred solution of the phosphazene. The mixture was heated to reflux for 2 weeks. The solids which precipitated from solution were filtered off and washed several times with THF (100 mL) and water (500 mL). The crude reaction mixture was dried under vacuum. Recrystallization from THF/*n*-hexane and acetone yielded the pure product (1.1 g, 31.4%).

**Synthesis of $N_3P_3[(NH)_2C_{14}H_8]_3$ (20).** A solution of hexachlorocyclotriphosphazene (**1**) (1.5 g, 0.0043 mol) in THF (100 mL) was added dropwise to a stirred solution of 9,10-diaminophenanthrene (3.1 g, 0.015 mol) and triethylamine (10 mL, 0.035 mol) in THF (200 mL). After the reaction mixture was heated to reflux and held there for 2 weeks, it was then filtered and washed three times with THF (200 mL), water (500 mL), acetone (500 mL), and HCl to remove the triethylamine hydrochloride quantitatively. Compound **20** (1.2 g, 31.8%) is a beige solid that is insoluble in most solvents.

**Acknowledgment.** This work was supported by the National Science Foundation Polymers Program Grant No. DMR 90-17366 and in part by the Dow Chemical Co. We also thank the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship to U.D.