The Tc-N(1) bond length of 2.145 (4) Å in (n-Bu_4N)[$TcCl_4$(abt)] indicates less multiple-bond character than is displayed in either the octahedral complex $Tc^{VI}(abt)_3$[13] or the square-pyramidal complex (n-Bu_4N)[$TcO(abt)_2$],[3] where the average Tc-N distances are 1.995 (11) and 2.08 (2) Å, respectively. This Tc^{V}-N bond length of 2.145 (4) Å is in good agreement with the average single-bond Tc-N distance of 2.125 (11) Å reported for the complex $[Tc(cyclam)O_2]^{+}$.[14] The Tc-S distance is reported to be 2.322 (2) Å. This value falls within the range of values reported for Tc^{V} square-pyramidal complexes and a Tc^{VI} octahedral abt complex. For the Tc^{V} complex (n-Bu_4N)[$TcO(abt)_2$][3] the average value of 2.30 (1) Å is reported, and a distance of 2.35 (10) Å is reported for the Tc^{VI} complex $Tc^{VI}(abt)_3$.[13]

Acknowledgment. We express our appreciation to Dr. Michael Clarke for his assistance with the magnetic susceptibility measurements. Mass spectral data were provided by the MIT Mass Spectrometry Facility, which is supported by NIH Grant No. RR00317 (to K. Biemann). This research was supported in part by USPHS Grant No. 5 R01 CA 34970 and DOE Grant No. DE-FG02-87ER60526.

Supplementary Material Available: Tables SI-SV, listing respectively complete X-ray data, atomic positional parameters including hydrogens and isotropic thermal parameters, anisotropic thermal parameters, intramolecular atomic distances, and intramolecular bond angles (13 pages); Table SVI, listing calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Synthesis of Cyclic Phosphazenes with Isothiocyanato, Thiourethane, and Thiourea Side Groups: X-ray Crystal Structure of $N_3P_3(NMe_2)_3(NCS)_3$

Harry R. Allcock,* J. Steven Rutt, and Masood Parvez

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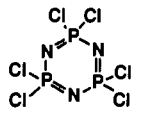
Reaction of the cyclic trimeric phosphazene $[NP(NCS)_2]_3$ with alcohols, ROH (R = CH_3, C_2H_5, 1-C_3H_7, 1-C_4H_9, and 2-C_3H_7), in THF resulted in the formation of thiourethane derivatives, $[NP(NHCSOR)_2]_3$, via a nongeminal reaction pathway. Reactions of $[NP(NCS)_2]_3$ with amines, RNH_2 (R = H, CH_3, C_6H_5, 1-C_4H_9, and 1-C_8H_{17}), in THF yielded thiourea derivatives, $[NP(NHCSNHR)_2]_3$. Interaction of the cyclic tetramer $[NP(NCS)_2]_4$ with alcohols and amines also yielded thiourethane and thiourea derivatives, although the reactivity of the tetramer was lower than that of the trimer. The reactivity of the isothiocyanato groups was influenced by the steric and electronic effects of cosubstituent side groups such as trifluoroethoxy or dimethylamino. X-ray crystallographic analysis of *cis*-nongeminal-$[NP(NMe_2)(NCS)]_3$ was carried out, and the structure was compared with those of $[NP(NCS)_2]_3$ and $[NP(NCS)_2]_4$. *cis*-nongeminal-$[NP(NMe_2)(NCS)]_3$ crystallized in the triclinic space group $P\bar{1}$. Unit cell parameters were a = 8.377 (7) Å, b = 9.030 (3) Å, c = 14.093 (7) Å, α = 85.55 (3)°, β = 74.91 (5)°, γ = 83.96 (4)°. The final R and R_w values were 0.047 and 0.074. The reactions of the cyclic phosphazenes served as models for those of the analogous macromolecular phosphazenes.

Cyclic and high-polymeric phosphazenes have been prepared that bear a wide variety of organic, organometallic, and inorganic side groups.[1-4] Hexachlorocyclotriphosphazene (**1**) and the cyclic tetrameric analogue **2** undergo a ring-opening polymerization when heated at 250 °C to form poly(dichlorophosphazene) (**3**), and the chloro units of species **1-3** can be replaced by organic side groups via nucleophilic replacement reactions.



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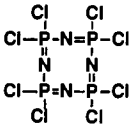

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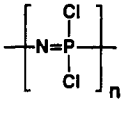
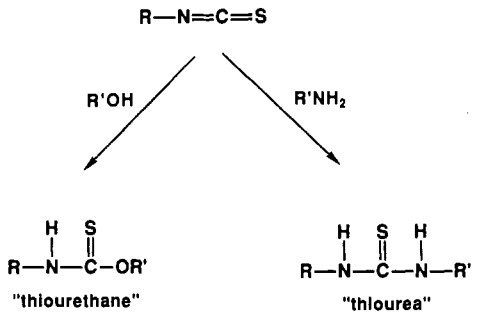


3

Small molecule phosphazenes such as **1** or **2** serve as small molecule models for the development of similar chemistry at the high-polymeric level.[5] Furthermore, X-ray diffraction studies of cyclic trimeric and tetrameric phosphazene species can provide clues to the electronic structure of the high polymers.[6] Mechanistic studies are more easily carried out with small-molecule species.

Scheme I



The focus of this paper is on the chemistry of cyclic phosphazene compounds that bear isothiocyanato side groups.[7,8] Isothiocyanates (R-NCS) have the ability to undergo addition reactions with alcohols and amines to form thiourethanes and thioureas (Scheme I). Thiourethane and thiourea linkages are characterized by hindered rotation about the C-N bonds caused by resonance effects.[9] Little is known about the properties of cyclic or high-

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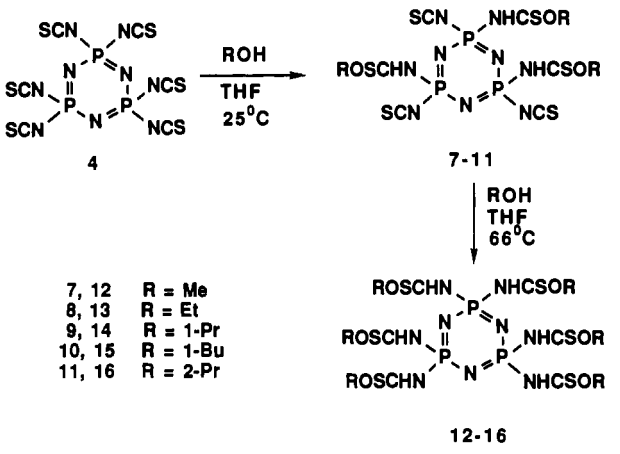
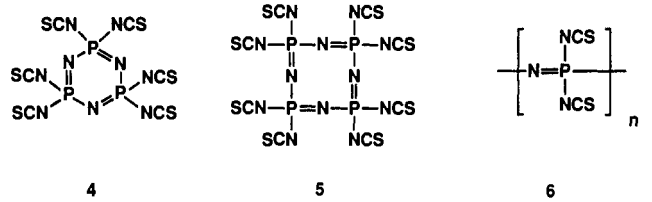
Scheme II



polymeric phosphazene compounds with thiourethane or thiourea side groups.

In 1958, Audrieth and co-workers reported the synthesis of the cyclic trimeric isothiocyanato phosphazene **4** and its tetrameric analogue **5** via side group replacement reactions between **1** or **2**

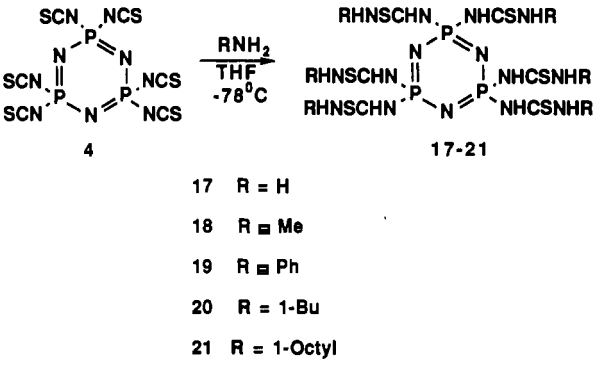


and potassium thiocyanate.[10,11] The results from that study also indicated that thiourethane or thiourea derivatives are formed when **4** and **5** react with alcohols or amines, although these species were not well-characterized. In addition, **4** and **5** were converted to a polymeric elastomer when heated at 145 °C. The product was believed to have the structure shown as **6**. This polymerization temperature is the lowest known for a cyclic phosphazene. Although brief reports of isothiocyanatophosphazene compounds have appeared since that time,[12-18] the chemistry of these species has not been developed systematically.

In principle, the addition reactions of isothiocyanato side groups with hydroxyl and amino compounds (Scheme I) should provide a useful method to link a variety of organic species, including bioactive compounds, to the phosphazene skeleton. Also, electronic coupling between the isothiocyanato side group and the unsaturated phosphazene backbone is of interest, and synthetic issues of ambidentate reactivity exist.[19] The P–NCS linkage bears two potential electrophilic sites, the phosphorous and carbon atoms, and the thiocyanate anion possesses two potential nucleophilic sites, the nitrogen or sulfur atoms.

In this paper, we have attempted to answer the following questions: (1) Does **4** react cleanly with alcohols and amines to form stable thiourethane and thiourea derivatives? (2) How does the electrophilic behavior of **4** compare to that of **5**? (3) Do cosubstituent side groups affect the electrophilicity of an isothiocyanato side group? (4) What information can be obtained from crystallographic analysis about isothiocyanato–phosphazene bonding? (5) In what ways might this model compound study be transposed to macromolecular phosphazenes?[20]

Scheme III



Results and Discussion

Reactions of 4 with Alcohols. Cyclic phosphazenes **4** and **5** were prepared by the reactions of $(NPCl_2)_3$ (**1**) or $(NPCl_2)_4$ (**2**) with potassium thiocyanate. Trimer **4** was then allowed to react with excess methanol, ethanol, 1-propanol, 1-butanol, and 2-propanol in THF at 66 °C to form stable thiourethane derivatives **12–16** (Scheme II). On the basis of ^{31}P NMR spectroscopic analysis of the reaction mixtures, the conversion of isothiocyanato side groups to thiourethane groups occurred via a nongeminal pathway. The partially reacted species **7–11** were detected as principle intermediates when the reactions were carried out at 25 °C. Higher temperatures (66 °C) were necessary to bring about reaction of all of the isothiocyanato groups of **7–11** to form **12–16**. The ability of the thiourethane side group to deactivate geminal isothiocyanato units was attributed to the steric bulk of the thiourethane side group. However, electronic effects may also play a role (see later). Thiourethanes **12–16** were stable to the atmosphere. Characterization data are discussed later.

Although species **12–16** were formed relatively easily (see Experimental Section), nonnucleophilic hydroxy compounds did not react with all the isothiocyanato side groups in **4**. For example, phenol failed to react with **4** in THF at 66 °C, and trifluoroethanol reacted with **4** very slowly in THF at 66 °C.

Reactions of 4 with Amines. Compound **4** was also allowed to react with several amines in THF at −78 °C to form thiourea derivatives **17–21** (Scheme III). However, the nongeminal addition pattern identified for thiourethane formation was not detected by ^{31}P NMR spectroscopic analysis for thiourea formation. Thioureas **17–21** were stable in the atmosphere. Characterization data are discussed in the next section.

Characterization of Thiourethanes and Thioureas. Thiourethanes **12–16** and thioureas **17–21** were characterized by a combination of multinuclear NMR, IR, and mass spectral data and elemental analysis (Table I). The ^{31}P NMR spectra consisted of singlet resonances for the ring phosphorus atoms. The ^{13}C NMR spectra consisted of resonances for the thiocarbonyl and alkyl carbon atoms in the side groups. The thiocarbonyl resonances were found in the region of δ = 190 ppm for the thiourethanes and δ = 180 ppm for the thioureas. The ^{1}H NMR, mass spectral, and elemental analysis data were consistent with the proposed structures. IR analysis showed bands for P–N (1200–1300 cm^{-1}), N–H (3100–3400 cm^{-1}), and aliphatic C–H (2800–3000 cm^{-1}) stretching modes. However, attempts to grow single crystals of **12–16** and **17–21** of suitable quality for X-ray crystallographic analysis were unsuccessful.

Reactivity of the Cyclic Tetramer versus the Cyclic Trimer. Thiourethane and thiourea derivatives of the cyclic tetramer **5** were also prepared. Cyclic tetramers are sometimes better models for phosphazene high polymers than are cyclic trimers.[5] Dif-

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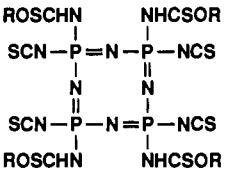
Table I. Characterization Data

compd	^{31}P NMR	^{1}H NMR (shift, ppm)	^{13}C NMR (shift, ppm)	MS calcd	MS exptl	anal., % element	anal., % calcd	anal., % found
12	singlet	CH_3 (3.96)	CH_3 (58.2)	675	675	C	21.31	21.01
	−7 ppm	NH (8.51)	CS (191.4)			H	3.55	3.50
						N	18.65	18.44
13	singlet	CH_3 (1.30)	CH_3 (14.2)	760	760	C	28.45	28.59
	−7 ppm	CH_2 (4.43)	CH_2 (69.3)			N	16.59	16.42
		NH (7.72)	CS (192.0)			H	4.78	4.81
14	singlet	CH_3 (1.04)	CH_3 (10.3)	843	843	C	34.15	34.00
	−7 ppm	CH_2 (1.52)	CH_2 (21.3)			H	5.73	5.91
		CH_2 (4.18)	CH_2 (72.8)			N	14.94	15.19
		NH (8.14)	CS (190.7)					
15	singlet	CH_3 (0.92)	CH_3 (13.8)	928	928	C	38.82	38.63
	−7 ppm	CH_2 (1.42)	CH_2 (19.3)			H	6.52	6.60
		CH_2 (1.74)	CH_2 (30.6)			N	13.59	13.74
		CH_2 (4.43)	CH_2 (72.2)					
		NH (9.25)	CS (191.2)					
16	singlet	CH_3 (1.31)	CH_3 (21.1)	843	843	C	34.14	34.41
	−7 ppm	CH (3.92)	CH (75.2)			H	5.69	5.49
		NH (8.50)	CS (189.6)			N	14.94	15.50
17	singlet	NH (6.61)	CS (176.0)	585	*a*	C	12.30	11.99
	−10 ppm					H	3.07	3.37
						N	35.86	35.44
18	singlet	CH_3 (4.01)	CH_3 (43.5)	669	*a*	C	48.40	48.29
	−18 ppm	NH (8.20)	CS (181.0)			H	4.06	4.09
						N	20.16	20.60
19	singlet	CH (6–8)	CH (138.7)	1041	*a*	C	21.52	21.99
	0 ppm	NH (6–8)	CH (128.4)			H	4.51	4.78
			CH (125.2)			N	31.38	31.00
			CH (123.9)					
			CS (179.7)					
20	singlet	CH_3 (0.93)	CH_3 (14.0)	921	*a*	C	39.06	39.12
	−4 ppm	CH_2 (1.37)	CH_2 (20.5)			H	7.23	7.01
		CH_2 (1.60)	CH_2 (30.1)			N	22.78	22.37
		CH_2 (3.54)	CH_2 (36.0)					
		NH (8.43)	CS (180.3)					
21	singlet	CH_3 (0.90)	CH_3 (14.1)	1257	*a*	C	51.52	51.88
	−4 ppm	CH_2 (1.30–1.60)	CH_2 (22.8)			H	9.13	9.40
		NH (8.31)	CH_2 (27.1)			N	16.69	16.39
			CH_2 (28.4)					
			CH_2 (28.7)					
			CH_2 (29.5)					
			CH_2 (32.0)					
			CH_2 (44.9)					
			CS (180.5)					
27	singlet	CH_3 (3.90)	CH_3 (58.4)	900	900	C	21.31	20.99
	−30 ppm	NH (8.50)	CS (191.9)			H	3.55	3.51
						N	18.65	18.02
28	singlet	CH_3 (1.31)	CH_3 (14.3)	1012	1012	C	28.45	28.39
	−27 ppm	CH_2 (4.39)	CH_2 (68.2)			H	4.78	4.90
		NH (7.60)	CS (191.3)			N	16.59	16.08
35	A_2B		NCS (144.5)	658	658	C	56.54	56.66
	δ_A = 7.4 ppm		CH (122.2)			H	3.83	4.01
	δ_B = −3.4 ppm		CH (127.1)			N	8.51	8.29
	J = 66 Hz		CH (130.8)					
			CH (151.7)					
36	A_2B		NCS (146.3)	688	688	C	19.20	19.25
	δ_A = 14.6 ppm		CH_2 (64, q)			H	1.46	1.33
	δ_B = 0.8 ppm		CF_3 (124, q)			N	8.14	8.35
	J = 94 Hz							
37	A_2B		NCS (143.2)	788		C	39.59	39.38
	δ_A = 15.0 ppm		CH_2 (72.0)			H	7.03	6.96
	δ_B = 0.3 ppm		CH_2 (71.1)			N	7.11	7.43
	J = 91 Hz		CH_2 (69.8)					
			CH_2 (67.0)					
			CH_3 (57.9)					
38	singlets		NCS (144.8)	441	441	C	24.29	25.38
	4.7, 4.1 ppm		CH_3 (37.0)			H	4.11	3.74
						N	28.57	28.35
39	multiplet	CH_3 (1.33)	CF_3 (125, q)	734	734	C	21.26	21.01
	17 ppm	CH_2 (4.28)	CH_2 (64, q)			H	2.20	2.25
		CH_2 (4.50)	CH_2 (69.7)			N	7.63	7.84
		NH (7.57)	CH_3 (14.8)					
			CS (190.8)					
41	multiplet	CH (6.6–8.5)	CS (183.0)	732	*a*	C	57.45	57.80
	6 ppm	CH_3 (1.02)	CH (152.1)			H	4.92	4.86
		CH_2 (1.43)	CH (131.2)			N	9.57	9.49
		CH_2 (1.60)	CH (127.4)					
		CH_2 (3.62)	CH (121.8)					
		NH (8.5)	CH_2 (36.1)					
			CH_2 (29.9)					
			CH_2 (20.4)					
			CH_3 (14.3)					
42	multiplet	CH_3 (1.10)	CF_3 (124, q)	761	*a*	C	23.65	23.68
	17 ppm	CH_2 (1.39)	CH_2 (64, q)			H	2.76	2.71
		CH_2 (1.70)	CH_3 (14.4)			N	9.20	8.99
		CH_2 (3.77)	CH_2 (21.0)					
		CH_2 (4.41)	CH_2 (29.5)					
		NH (8.11)	CH_2 (38.1)					
			CS (182.0)					
43	multiplet	CH_2 (3.4–4.3)	CH_3 (13.5)	868	*a*	C	41.81	41.50
	18 ppm	CH_3 (1.02)	CH_2 (21.0)			H	7.72	7.39
		CH_2 (1.43)	CH_2 (29.4)			N	8.13	8.51
		CH_2 (1.85)	CH_2 (35.9)					
		NH (7.43)	CH_2 (71.5)					
			CH_2 (70.9)					
			CH_2 (69.4)					
			CH_2 (66.9)					
			CH_3 (57.6)					
			CS (181.4)					

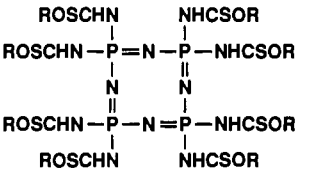
32	singlet	CH (6–8)	CH (138.0)	1012	*a*	C	48.40	48.29	**44**	singlet	CH_3 (2.67)	CH_3 (13.7)	441	*a*	C	38.16	38.01
	–20 ppm	NH (6–8)	CH (127.6)			H	4.06	4.39		11, 10	NH (8.31)	CH_2 (20.0)			H	7.72	7.98
			CH (124.3)			N	20.16	20.33		ppm	CH_3 (0.94)	CH_2 (30.7)			N	25.44	25.80
			CH (120.9)								CH_2 (1.40)	CH_2 (36.4)					
			CS (180.1)								CH_2 (1.60)	CH_3 (45.8)					
33	singlet	CH_3 (0.90)	CH_3 (14.0)	1228	*a*	C	39.06	39.41			CH_2 (3.59)	CS (181.7)					
	–22 ppm	CH_2 (1.40)	CH_2 (19.8)			H	7.23	7.01									
		CH_2 (1.61)	CH_2 (29.9)			N	22.78	22.60									
		CH_2 (3.49)	CH_2 (36.1)														
		NH (8.40)	CS (181.0)														
34	singlet	CH_3 (0.91)	CH_3 (14.1)	1676	*a*	C	51.52	51.19									
	–19 ppm	CH_2 (1.33–1.66)	CH_2 (23.1)			H	9.13	8.99									
		CH_2 (3.58)	CH_2 (27.5)			N	16.69	16.60									
		NH (8.27)	CH_2 (29.0)														
			CH_2 (29.8)														
			CH_2 (29.8)														
			CH_2 (32.3)														
			CH_2 (45.8)														
			CS (180.8)														

[a] Molecular ions of the thioureas could not be detected by mass spectrometric analysis.

ferences between the reactivity of the trimer and tetramer were detected, with the tetramer being less reactive than the trimer. As with the trimer reactions, interactions of **5** with an excess of methanol, ethanol, 1-propanol, 1-butanol, or 2-propanol in THF at 25 °C proceeded in a nongeminal pattern, and species **22–26** were detected by ^{31}P NMR analysis as primary reaction intermediates. The fully reacted methanol and ethanol derivatives **27** and **28** were formed in THF at 66 °C, but complete reaction of



22-26



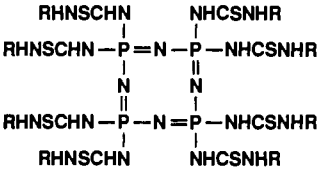
27-31

22, 27 R = Me
23, 28 R = Et
24, 29* R = 1-Pr
25, 30* R = 1-Bu
26, 31* R = 2-Pr

(Species 29-31 were not formed under the mild reaction conditions employed)

5 with 1-propanol, 1-butanol, or 2-propanol to form **29–31** in THF at 66 °C could not be achieved. The reduced electrophilicity of the tetramer relative to the trimer is probably due to a greater degree of steric crowding between the side groups linked to the puckered ring.[11] However, the tetramer ring is also more flexible than that of the trimer. Electronic effects may also play a role in the reduced electrophilicity of the tetramer (see later). Characterization data for **27** and **28** are given in Table I.

Reactions of **5** with aniline, 1-butylamine, and 1-octylamine in THF at −78 °C to form **32–34** were also carried out. All the isothiocyanato side groups reacted with the amines, perhaps due

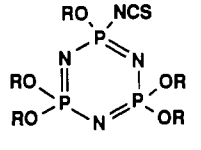


32-34

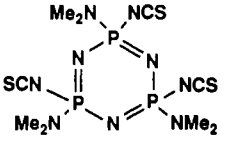
32 R = Ph
33 R = 1-Bu
34 R = 1-Octyl

to the higher nucleophilicity of the amines. A nongeminal addition process was not detected for the amine reactions, and this agrees with the results for the trimer chemistry. Characterization data for **32–34** are given in Table I.

Effect of Cosubstituent on Electrophilic Reactivity. Mixed-substituent isothiocyanatocyclotriphosphazenes **35–38** were prepared in order to probe the influence of cosubstituent side groups



35-37



38

35 R = Ph

36 R = CH_2CF_3

37 R = $CH_2CH_2OCH_2CH_2OCH_3$

on the reactivity of the isothiocyanato groups. The four cosubstituent groups (phenoxy, trifluoroethoxy, 2-(2-methoxyethoxy)ethoxy, and dimethylamino) were chosen because of their widespread use in macromolecular phosphazene chemistry and

Table II. Summary of Crystal Data for **38**

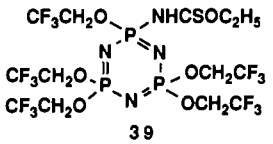
formula	$C_9H_{18}N_9P_3S_3$	λ, Å	0.71073
fw	441	*T*, K	140
space group	$P\bar{1}$	scan method	$\omega/2\theta$
		ω-scan width, deg	(0.70 + 0.35 tan θ)
cryst syst	triclinic		
a, Å	8.377 (7)	cryst decay	2.6%
b, Å	9.030 (3)	anisotropic decay cor	
c, Å	14.093 (7)	min.	0.9636
α, deg	85.55 (3)	max.	1.0583
β, deg	74.91 (5)	no. of unique data measd	2807
γ, deg	83.96 (4)	no. of data used [$I > 3\sigma(I)$]	2625
V, Å^3	1022.1	data:param ratio	9.7
Z	2	R, R_w ($=(\sum\Delta^2/\sum wF_o^2)^{1/2}$)	0.047, 0.074
D(calcd), g/cm^3	1.434	$(\Delta/\sigma)_{max}$ in last cycle	<0.2
radiation	Mo Kα	$\Delta\rho$, e Å^{-3} in final ΔF map	0.35
θ limits, deg	2–25	final *p* param in wt scheme	0.080
		goodness of fit	1.838
μ, cm^{-1}	5.918		

their varying steric and electronic characteristics. The syntheses of **35–38** were also carried out to examine ambidentate reactivity and to prepare isothiocyanato derivatives for X-ray crystallographic analysis.

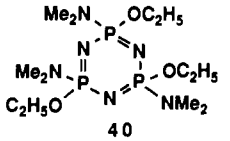
Although **4** reacted rapidly with ethanol in THF at 25 °C, no reaction was detected by ^{31}P NMR spectroscopic analysis between **35–37** or **38** and excess ethanol in THF at 25 °C. This implies that steric hindrance generated by bulky cosubstituent side groups reduces the reactivity of the isothiocyanato side group. This was found to be the case irrespective of whether the cosubstituent side group was electron-withdrawing (e.g. trifluoroethoxy, **36**) or electron-releasing (e.g. dimethylamino, **38**).

However, a difference in reactivity was detected between **36** and **38**, which implies that electronic effects generated by the cosubstituent side groups may also be important. Reaction of **36** with excess ethanol in THF at 66 °C resulted in the formation of the thiourethane derivative **39**. However, reaction of **38** with ethanol in THF at reflux yielded the alkoxy derivative **40** rather than a thiourethane derivative. The ^{31}P NMR spectral analysis of the reaction mixture for the synthesis of **40** suggested that the isothiocyanato side groups were converted first to thiourethane side groups and that ethanol then displaced the thiourethane side groups (see Experimental Section). Thus, an electron-releasing cosubstituent (dimethylamino) appears to increase the ability of the thiourethane side group to act as a leaving group.

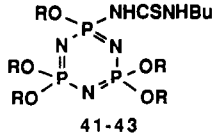
Thiourea derivatives **41–44** were formed by the reactions of **35–38** with 1-butylamine in THF at 25 °C. Characterization data for **35–44** are given in Table I. Characterization data for **40** have been reported previously.[21]



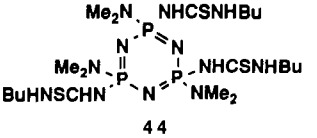
39



40



41-43



44

41 R = Ph

42 R = CH_2CF_3

43 R = $CH_2CH_2OCH_2CH_2OCH_3$

X-ray Structural Analysis of $[NP(NMe_2)(NCS)]_3$. An X-ray crystallographic analysis of **38** was carried out, and the X-ray structure was compared with those of **4**[17] and **5**[18] reported in the literature. A summary of cell constants and data collection parameters is given in Table II, the ORTEP diagram is shown in Figure 1, and bond lengths, bond angles, and positional parameters are presented in Tables III–V. Analysis of the structural data confirmed that important electronic interactions exist between the isothiocyanato side group and the phosphazene ring.

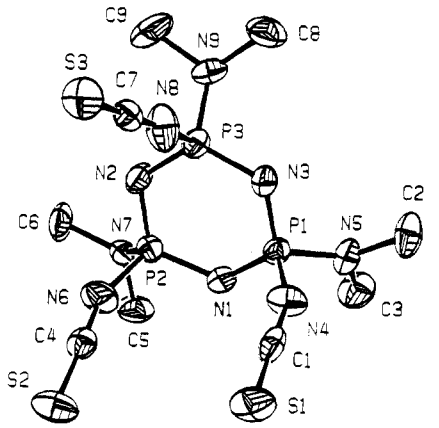


Figure 1. ORTEP diagram for $[NP(NMe_2)(NCS)]_3$ (**38**).

Table III. Selected Bond Distances for **38** (Å)

S1–C1	1.588 (2)	P3–N3	1.581 (2)
S2–C4	1.549 (2)	P3–N8	1.680 (2)
S3–C7	1.543 (3)	P3–N9	1.620 (2)
P1–N1	1.588 (1)	N4–C1	1.180 (3)
P1–N3	1.581 (1)	N5–C2	1.456 (3)
P1–N4	1.692 (2)	N5–C3	1.445 (3)
P1–N5	1.609 (2)	N6–C4	1.185 (3)
P2–N1	1.585 (2)	N7–C5	1.470 (2)
P2–N2	1.575 (2)	N7–C6	1.470 (3)
P2–N6	1.698 (2)	N8–C7	1.193 (3)
P2–N7	1.623 (2)	N9–C8	1.479 (3)
P3–N2	1.580 (2)	N9–C9	1.463 (3)

Table IV. Selected Bond Angles for **38** (deg)

N1–P1–N3	117.97 (8)	N2–P3–N9	110.17 (9)
N1–P1–N4	108.93 (9)	N3–P3–N8	106.3 (1)
N1–P1–N5	109.73 (9)	N3–P3–N9	109.66 (9)
N3–P1–N4	103.40 (9)	N8–P3–N9	104.7 (1)
N3–P1–N5	112.04 (9)	P1–N1–P2	120.12 (9)
N4–P1–N5	103.55 (9)	P2–N2–P3	120.48 (9)
N1–P2–N2	119.01 (8)	P1–N3–P3	121.57 (9)
N1–P2–N6	106.98 (9)	P1–N4–C1	156.1 (2)
N1–P2–N7	109.72 (9)	P2–N6–C4	158.5 (2)
N2–P2–N6	105.3 (1)	P3–N8–C7	167.8 (2)
N2–P2–N7	109.84 (8)	S3–C7–N8	177.8 (2)
N6–P2–N7	104.95 (9)	S2–C4–N6	178.0 (2)
N2–P3–N3	118.88 (8)	S1–C1–N4	178.0 (2)
N2–P3–N8	106.1 (1)		

It should be noted that, like halogeno units, the isothiocyanato group is considered to be an electron-withdrawing group that functions mainly through inductive effects. However, it can also be electron-releasing via resonance effects. Several different Lewis structures are believed to contribute to the bonding of the isothiocyanato group, and donation from a lone electron pair on nitrogen into the R group of a R–NCS linkage is possible (see structures **45** and **46**). Donation of the lone electron pair into

Lewis Structures

45 **46**

the phosphazene ring (structure **46**) should, in principle, increase the electrophilicity of the carbon atom of the isothiocyanato side group. The phosphazene ring is a strong electron-withdrawing group, which should facilitate acceptance of the lone electron pair

(21) Allcock, H. R.; Desorcie, J. L.; Wagner, L. J. *Inorg. Chem.* **1985**, *24*, 333.

Table V. Positional Parameters for **38**

atom	x	y	z
S1	0.65229 (9)	0.45214 (7)	0.56684 (6)
S2	0.38523 (10)	0.43627 (7)	0.86764 (6)
S3	0.34888 (9)	−0.22498 (8)	0.69522 (5)
P1	0.97695 (8)	0.12074 (6)	0.68316 (4)
P2	0.79212 (8)	0.09525 (6)	0.87473 (4)
P3	0.81931 (8)	−0.13393 (6)	0.75357 (4)
N1	0.9237 (3)	0.1778 (2)	0.7916 (1)
N2	0.7537 (3)	−0.0665 (2)	0.8581 (1)
N3	0.9296 (3)	−0.0387 (2)	0.6670 (1)
N4	0.8802 (3)	0.2359 (2)	0.6110 (2)
N5	1.1706 (3)	0.1407 (2)	0.6356 (1)
N6	0.6082 (3)	0.2007 (2)	0.8892 (2)
N7	0.8390 (3)	0.0970 (2)	0.9793 (1)
N8	0.6498 (3)	−0.1630 (3)	0.7172 (2)
N9	0.9126 (3)	−0.2986 (2)	0.7633 (1)
C1	0.7805 (3)	0.3291 (2)	0.5936 (2)
C2	1.2448 (4)	0.1059 (3)	0.5336 (2)
C3	1.2726 (4)	0.2203 (3)	0.6790 (2)
C4	0.5137 (3)	0.3044 (2)	0.8795 (2)
C5	0.9008 (4)	0.2318 (2)	1.0040 (2)
C6	0.7378 (4)	0.0150 (3)	1.0639 (2)
C7	0.5181 (3)	−0.1917 (2)	0.7092 (1)
C8	0.9984 (4)	−0.3736 (3)	0.6720 (1)
C9	0.8399 (5)	−0.4025 (3)	0.8440 (3)

from the exocyclic nitrogen atom. For related trimers and tetramers, $(NPX_2)_3$ and $(NPX_2)_4$, that possess side groups (X) that donate electron density into the ring, the relative amount of lone-pair donation by a side group into the ring may be different for trimers and tetramers.[6]

The reported structures for **4** and **5** suggest that a number of possible electronic arrangements contribute to bonding in isothiocyanatophosphazenes and that structures **45** and **46** contribute strongly. The average exocyclic P–N bond lengths reported for **4** and **5** are 1.63 (2) and 1.644 (14) Å, respectively. These appear to be shorter than the average exocyclic P–N bond length in $[NP(NMe_2)_2]_3$ (1.652 (4) Å), a compound in which significant lone-pair donation occurs from the exocyclic nitrogen atoms into the phosphazene ring.[22,23]

Analysis of the X-ray structure of **38** indicates that the average exocyclic P–N bond length for the isothiocyanato side groups is 1.690 (9) Å, which is longer than those reported for **4** or **5**. On the other hand, the average exocyclic P–N bond length for the dimethylamino side groups of **38** is 1.617 (7) Å, which is shorter than the value in $[NP(NMe_2)_2]_3$.[22] Thus, the electron-releasing dimethylamino group supplies electron density to the phosphazene ring, while the isothiocyanato group withdraws electron density from the ring. The overall result is that the geminal dimethylamino group may reduce the contribution of structure **46** for the isothiocyanato group. This "push–pull" electronic effect, together with steric effects, could help to reduce the electrophilicity of **38** relative to that of **4**. The cyclotriphosphazene ring in **38** was found to exist in a half-chair conformation, with N(1) 0.323 Å out of the plane of the phosphazene ring.[24]

Regioselectivity for Ambidentate Reactions. Halogenated phosphazene electrophiles such as **1–3** are "hard", according to classical hard–soft acid–base principles,[25] due to the positive charge on the phosphorus atoms. This is consistent with the ability of the thiocyanate anion to react with these compounds to yield *iso*thiocyanato derivatives (P–NCS) rather than thiocyanato derivatives (P–SCN) (the nitrogen atom in the $(SCN)^-$ unit is the "hard" nucleophilic site). In principle, **4** and **5** are also ambidentate electrophiles, since a partial positive charge exists on both the phosphorus and carbon atoms. However, contribution of structure **46** should favor nucleophilic attack at carbon relative to phosphorus, and indeed, carbon was clearly the preferred site of attack.

Implications for Polymer Synthesis. Stable thiourethane and thiourea derivatives of phosphazenes can clearly be formed at the small molecule level. In principle, high-polymeric thiourethanes, $[NP(NHCSOR)_2]_n$, and thioureas, $[NP(NHCSNHR)_2]_n$, should be accessible via the addition reactions of **6** with alcohols and amines. However, the model reactions of the tetramer **5** with alcohols suggest that steric and electronic effects could impair the synthesis of thiourethane derivatives from **6**. By contrast, the reactions of **5** with amines suggest that thiourea derivatives of **6** should be accessible. Mixed-substituent polymers that possess electron-withdrawing trifluoroethoxy cosubstituent groups may also be accessible.

Experimental Section

Materials. A mixture of **1** and **2** was obtained from Ethyl Corp. Compound **1** was purified by recrystallization from hexane and **2** by recrystallization from heptane. Potassium thiocyanate (Aldrich) was dried at 105 °C under vacuum for 24 h and was stored in a drybox. 18-Crown-6 ether (Aldrich) was recrystallized from acetonitrile and was stored in a dry box. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen. Methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, and trifluoroethanol (Aldrich) were distilled from barium oxide and stored over molecular sieves. Phenol (Aldrich) was sublimed and stored in a dessicator. Aniline and 1-butylamine were fractionally distilled from calcium hydride and were stored over molecular sieves. Anhydrous ammonia (Linde, Union Carbide) and monomethylamine (Matheson) were used as received. 1-Octylamine (Aldrich) was stored over molecular seives. Species $N_3P_3(OC_6H_5)_5Cl$,[26] $N_3P_3(OCH_2CF_3)_5Cl$,[27] and *trans*-nongeminal-$[NP(NMe_2)Cl]_3$[28] were prepared by literature procedures. The synthesis of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_5Cl$ was carried out by a modified literature method[26] by the reaction of **1** with 5 equiv of the sodium salt of 2-(2-methoxyethoxy)-ethanol.

Instrumentation and Methods. All reactions were carried out with the use of conventional inert-atmosphere techniques. ^{31}P and ^{13}C NMR spectra were obtained with the use of a JEOL FX90Q spectrometer, and high-field ^1H NMR and ^{13}C NMR spectra, with the use of a Bruker WP-360 spectrometer. Infrared spectra were obtained with the use of a Perkin-Elmer 1710 FT-IR instrument. Samples were analyzed as KBr pellets or as oils between NaCl disks. Fast-atom bombardment (FAB) mass spectra were obtained with the use of a Kratos MS50Te spectrometer operated in the positive ionization mode with a 2-nitrophenyl octyl ether matrix. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Synthesis of $[NP(NCS)_2]_3$ (4). An improvement to several literature procedures was developed.[11,16] A flask was charged with a mixture of **1** (100 g, 0.287 mol), potassium thiocyanate (200 g, 2.06 mol), and 18-crown-6 ether (0.50 g, 2.0 mmol) as a phase-transfer agent. Tetrahydrofuran (THF) (600 mL) was added, and the reaction mixture was refluxed gently for 24 h. Most of the THF was removed by rotary evaporation with minimal application of heat, and the residual THF was removed on a vacuum line to yield a yellow powder. The powder was extracted thoroughly with heptane (2 L), and the heptane extract was filtered to remove insoluble salts. Cooling the heptane extract to −55 °C over a period of several days yielded **4**, which was isolated by filtration. Several more recrystallizations of **4** from heptane at −55 °C were carried out to remove traces of a yellow impurity. Compound **4** could be purified further from the yellow impurity by passing a heptane solution of **4** through a Florosil column, or by rapid extraction of crystals of **4** with cold acetone which quickly dissolved the impurity in preference to the target compound. The yields were typically 40–60%. Compound **4** was stored under vacuum or in a dry box. Compound **4** is sensitive to a high humidity atmosphere.

Synthesis of $[NP(NCS)_2]_4$ (5). A similar method was used to prepare **5**. The cyclic tetramer **5** is much less soluble in heptane and other organic solvents than is the trimer, and this necessitated some procedural modifications. A flask was charged with a mixture of tetramer **2** (32 g, 0.069 mol), potassium thiocyanate (65 g, 0.67 mol), and 18-crown-6 ether

(22) Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1973**, *51*, 1295.
(23) More lone-pair donation from the side group may occur for $[NP(NMe_2)_2]_3$ than for $[NP(NMe_2)_2]_4$ (see ref 6).
(24) It should be noted that the crystal of **14** selected for X-ray analysis showed the cis configuration, while the trans isomer of $N_3P_3(NMe_2)_3Cl_3$ was used to make **14**.
(25) Pearson, R., Ed. *Hard Soft Acids and Bases*; Dowden, Hutchinson, and Ross: Stroudsberg, PA, 1973.
(26) McBee, E. T.; Okuhara, K.; Morton, C. J. *Inorg. Chem.* **1966**, *5*, 450.
(27) Allcock, H. R.; Mang, M. N.; McDonnell, G. S.; Parvez, M. *Macromolecules* **1987**, *20*, 2060.
(28) Keat, R.; Shaw, R. A.; *J. Chem. Soc.* **1965**, 2215.
(29) Allcock, H. R.; Rutt, J. S.; Welker, M. F.; Parvez, M. To be submitted for publication in *Inorg. Chem.*

(0.25 g, 1.0 mmol). THF (200 mL) was added, and the reaction mixture was stirred at a gentle reflux temperature for 24 h. Solvent was removed by rotary evaporation, and the residue was dried under vacuum. The residue was extracted with *hot* heptane (1 L), and the heptane extract was filtered and cooled to −55 °C for several days to precipitate the tetramer. Rapid extraction of **5** with cold acetone dissolved traces of a yellow impurity. Alternatively, filtration of a chloroform solution of **5** through Florosil further purified **5** from traces of the yellow impurity.

Reactions of 4 with Alcohols. The reaction of **4** with ethanol is typical. Compound **4** (1.0 g, 2.1 mmol) was dissolved in THF (15 mL), and ethanol (20 mL) was added. The progress of the reaction was monitored by ^{31}P NMR spectroscopic analysis. The partially reacted species **8** was formed rapidly at 25 °C, but full reaction to form **13** did not occur at room temperature after 24 h. Reflux of the mixture for 24 h yielded **13**. Volatile species were removed under vacuum to leave **13** in quantitative yield. Extensive drying of the thiourethane derivatives under high vacuum with warming was necessary to remove all volatile species. The yields of **12–16** were quantitative. The intermediate species **7–11** were detected by ^{31}P NMR spectroscopic analysis as singlet resonances at δ = −12 ppm.

Reactions of 4 with Amines. The reaction of **4** with ammonia is typical. Compound **4** (1.0 g, 2.1 mmol) was dissolved in THF (15 mL). The flask was cooled to −78 °C, and ammonia (20 mL) was condensed into the flask. The reaction mixture was allowed to warm to room temperature over a period of several hours as excess ammonia boiled off. Volatile species were removed under vacuum to yield the product. Extensive drying of the products under high vacuum with gently warming was necessary to remove all the volatile species. The thiourea derivative, **17**, was soluble in water. The yields of **17–21** were quantitative. It should be noted that although an excess of amine was used for the synthesis of **17–19**, the syntheses of **20** and **21** were carried out with the use of only 1 equiv of amine per equivalent of isothiocyanato side group. This was because further reactions were detected between **20** and **21** and 1-butylamine and 1-octylamine in THF solution.

Reaction of 5 with Alcohols and Amines. Analogous procedures were used for both the trimer and tetramer reactions. Progress of the reaction was monitored by ^{31}P NMR spectroscopic analysis. Intermediate species **22–26** were identified by singlets at δ = −36 ppm. Reaction of **5** with methanol to form **27** in refluxing THF was complete after 2 days. The reaction with ethanol was complete only after 5 days at reflux. ^{31}P NMR spectroscopic analysis showed that no further reaction of **5** with 1-propanol, 1-butanol, or 2-propanol occurred after 5 days at reflux temperature. The synthesis of **18** and **19** was carried out with the use of only 1 equiv of amine per equivalent of isothiocyanato side group. The yields of the tetramers were quantitative.

Synthesis of $N_3P_3(OC_6H_5)_5(NCS)$ (35). Monochloropentakis(phenoxy)cyclotriphosphazene (1.3 g, 2.0 mmol) was dissolved in acetonitrile (25 mL) and was allowed to react with potassium thiocyanate (5.0 g, 52 mmol) in the presence of 18-crown-6 ether (0.1 g, 0.4 mmol) or Bu_4NBr at reflux temperature for 7–14 days. Bu_4NBr was found to be the more effective phase-transfer agent. Solvent was removed by rotary evaporation, and the residue was extracted with methylene chloride. The extract was filtered through fuller's earth, and solvent was removed by rotary evaporation to yield the product. Compound **35** was recrystallized from hexane and was stored in a drybox.

Synthesis of $N_3P_3(OCH_2CF_3)_5(NCS)$ (36). Monochloropentakis(trifluoroethoxy)cyclotriphosphazene (1.3 g, 2.0 mmol) was dissolved in acetonitrile (30 mL) and was allowed to react with potassium thiocyanate (0.4 g, 4 mmol) in the presence of 18-crown-6 ether (0.1 g, 0.4 mmol) at 45 °C for 48 h. The product was isolated by the same methods used for **35**. Compound **36** was an oil that hydrolyzed slowly in the air but was stable if stored in a drybox.

Synthesis of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_5(NCS)$ (37). The compound $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_5Cl$ (2.0 g, 2.6 mmol) was dissolved in THF (25 mL) and was allowed to react with potassium thiocyanate (0.5 g, 5.2 mmol). No reaction was detected at room temperature. At reflux temperature, the substitution reaction was complete after 24 h. Volatile species were removed by rotary evaporation, and the residue was extracted with methylene chloride and filtered through fuller's earth. Methylene chloride was removed by rotary evaporation to yield **37**. Compound **37** was sensitive to the atmosphere over extended periods of time, but could be stored without decomposition in the drybox.

Synthesis of $[NP(NMe_2)(NCS)]_3$ (38). *trans*-nongeminal-$[NP(NMe_2)Cl]_3$ (4.0 g, 0.011 mol) was dissolved in acetonitrile (25 mL) and was allowed to react with potassium thiocyanate (10 g, 0.10 mol) and 18-crown-6 ether (0.1 g, 0.4 mmol) at reflux temperature for 7 days. The product was isolated by the same methods used to obtain **35–37**. It was recrystallized from hexane. Decomposition occurred during extended exposure to the atmosphere, but **38** could be stored in the drybox.

Reactions of 35–38 with Ethanol and 1-Butylamine. In each case, the cyclotriphosphazene (0.5 g) was dissolved in THF (2 mL), and ethanol or 1-butylamine (1 mL) was added. No reactions with ethanol at 25 °C were detected by ^{31}P NMR analysis. The addition reactions with 1-butylamine were complete in 15 min at 25 °C. Removal of the volatile species under vacuum afforded the thiourea derivatives **41–44** in quantitative yields. Compounds **36** and **38** were allowed to react with excess ethanol in THF at reflux temperature to form **39** and **40**. Removal of volatile components under vacuum yielded **39** and **40** in quantitative yields. Compound **40** was purified further by chromatography (silica, hexane/methylene chloride).

The reaction of **38** with ethanol was monitored by ^{31}P NMR spectroscopic analysis. In the early stages of the reaction, a singlet at δ = 15 ppm was detected as a primary product. This is believed to correspond to the thiourethane compound, $[NP(NMe_2)(NHCSOEt)]_3$. However, with further reaction, this singlet was replaced with a new singlet at δ = 25 ppm. The new spectrum corresponded to that of **40**.

Ambidentate Reactions. These reactions were monitored by ^{31}P NMR spectroscopic analysis. Hexabromocyclotriphosphazene $(NPBr_2)_3$[33] was found to react with potassium thiocyanate in THF at 66 °C to yield **4**. However, hexafluorocyclotriphosphazene $(NPF_2)_3$ did not react with potassium thiocyanate in THF. Sodium thiocyanate reacted with **1** to yield **4**. Ammonium thiocyanate cannot be used for the synthesis of **4** due to a reaction of **4** with thiocyanic acid/ammonia ($HNCS/NH_3$). Mercury(II) thiocyanate and copper(I) thiocyanate did not react with **1**.

X-ray Structural Characterization of 38. Single crystals of **38** suitable for crystallographic analysis were grown by the slow evaporation of a hexane solution of **38**. Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf-Nonius CAD4 diffractometer by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected by the $\omega/2\theta$ scan method using monochromatized radiation in the range $2° < \theta < 25°$. The intensities of three reflections, chosen as standards, were monitored at regular intervals. These decreased by 2.6% over the course of the data collection; this decay was corrected for by appropriate scaling. Intensities of 2807 unique reflections were measured, of which 2625 had $I > 3\sigma(I)$, and were used in the structure solution and refinement. Data were corrected for Lorentz and polarization factors; absorption correction was considered to be unnecessary.

The structure was solved by direct methods. Refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the nonhydrogen atoms. At an intermediate stage in the refinement, a difference map revealed all of the hydrogen atoms, which were included in the subsequent cycles of refinement with an overall fixed temperature factor. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann,[30] and of Stewart, Davidson, and Simpson[31] and allowance was made for anomalous dispersion.[32] A difference map calculated at the conclusion of the refinement showed no significant unusual features. All computer programs were part of the Enraf-Nonius Structure Determination Package (SDP Plus, Version 3.0), Enraf-Nonius, Delft, Holland, 1982, and were implemented on a PDP 11/44 computer.

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Supplementary Material Available: Tables of bond lengths, bond angles, positional parameters, thermal parameters, and least-squares planes (6 pages); a table of observed and calculated structure factor amplitude data (27 pages). Ordering information is given on any current masthead page.

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