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Synthesis and Structure of Nongeminally Substituted Cyclic Phosphazenes with Haloalkyl and Thioester Functional Groups

June-Ho Jung, Srinagesh K. Potluri, Hongming Zhang, and Patty Wisian-Neilson*

Department of Chemistry, Southern Methodist University, Dallas, Texas 75275-0314

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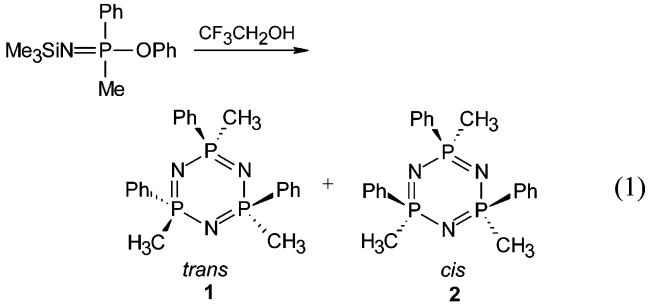
Nongeminally substituted cyclic phosphazenes with various haloalkyl substituents were prepared using deprotonation–substitution reactions at the methyl groups of the cis isomers of nongeminally substituted *cis*-$[Me(Ph)P{=}N]_3$, **2.** Treatment of **2** with *n*-BuLi followed by reaction with organic halogenated reagents (RX = C_2Cl_6, $BrC(O)CMe_2Br$, and ICH_2COOEt) at low temperature afforded the various cyclic derivatives *cis*-$[(XCH_2)(Ph)PN]_3$ (**3**, X = Cl, **4**, Br, and **5**, I). The mono- and dibromoalkyl derivatives, *cis*-$[Ph_3(BrCH_2)Me_2P_3N_3]$, **6**, and $[Ph_3(BrCH_2)_2MeP_3N_3]$, **7**, were also isolated along with **4** when the electrophile was dibromoethane. Reaction of *cis*-$[Ph(BrCH_2)PN]_3$, **4**, with KSC(O)Me gave *cis*-$[Ph(MeC(O)SCH_2)PN]_3$, **8**. The structures of all the cis cyclic phosphazenes were determined by NMR spectroscopy and X-ray diffraction. All retained the basketlike shape with the hydrophobic phenyl groups opposite the haloalkyl groups on the P_3N_3 ring. Thermal analysis of the new cyclic trimers indicates that ring-opening polymerization does not occur. The melting points and the thermal stabilities of haloalkyl cyclophosphazenes were higher than those of the parent compound **2**.

Introduction

Phosphazenes, $[RR'PN]_n$, are either cyclic or polymeric compounds based on alternating phosphorus and nitrogen atoms in rings or chains. The types of substituents at phosphorus are widely varied and account for a diverse range of properties for both the cyclic and polymeric systems.[1] Recently, we reported the preparation, isolation,[2] and reactivities[3,4] of the cis and the trans isomers of the nongeminally substituted methylphenylphosphazene, $[Me(Ph)PN]_3$, which were prepared by treatment of the phosphoranimine $Me_3SiN{=}P(OPh)(Me)(Ph)$ with CF_3CH_2OH (eq 1). Thermolysis of **1** and **2** resulted in equilibrium mixtures of the trimer and all four isomers of the corresponding tetramer, $[Me(Ph)PN]_4$.[3] The cis structure **2** and the cone structure of the tetramer $[Me(Ph)PN]_4$,[3] with all phenyl groups on the same side of the PN rings, have been compared to the basket-shaped calixarenes[5] or cyclodextrins.[6] Given the extensive chemistry of these two classes of organic molecules and their applications as biological and chemical sensors, catalysts, and nanomaterials, this analogy implies that simple derivative chemistry of the nongeminally substituted methylphenyl cyclophosphazenes will provide access to new basketlike inorganic molecules with interesting properties.



(1)

Although the deprotonation−substitution reactions on polyphosphazenes with P−C bonded substituents (e.g., poly(methylphenylphosphazene), $[(Me)(Ph)PN]_n$) have been well studied, the lack of availability of the nongeminally substituted compounds has precluded such studies on the cyclic

* Author to whom correspondence should be addressed. E-mail: pwisian@mail.smu.edu.

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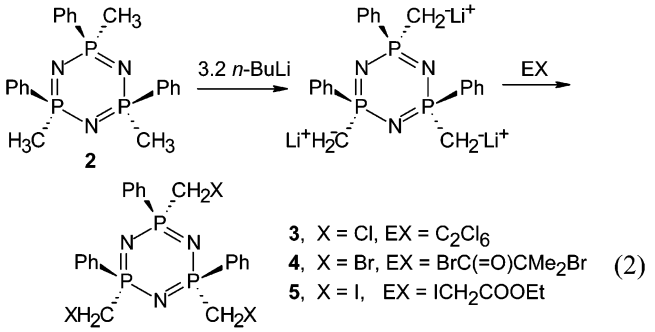
analogues, $[Me(Ph)PN]_3$, **1** and **2**. Now that these are readily available, we have shown that the P-methyl group in both **1** and **2** can be deprotonated, then treated with MeI to give *trans*- and *cis*-$[Et(Ph)PN]_3$,[4] respectively, without significantly changing the geometry around the P_3N_3 ring. On the basis of these results, the controlled stereochemistry of the isomers, and the potential utility of these basket-shaped molecules, we are exploring the feasibility of using the relatively planar PN ring system as a platform for synthesizing more complex molecules that might act as receptors, self-assembling systems, bioactive molecules, and various types of sensors. We report here the synthesis of a new series of nongeminal haloalkyl-substituted cyclophosphazene trimers via deprotonation−substitution reactions of *cis*-$[Me(Ph)PN]_3$. The reactions with nucleophiles, thermal stability, and solid-state structures are also presented.

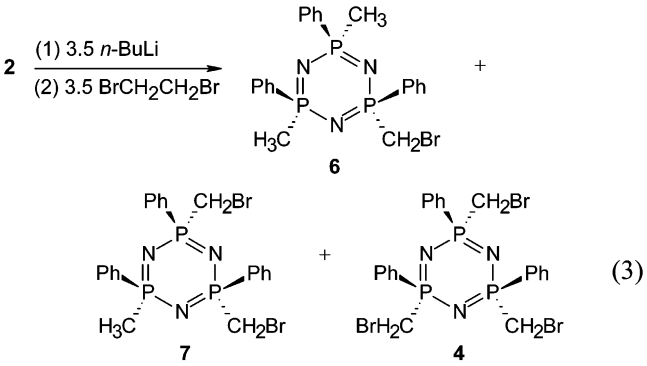
Results and Discussion

The deprotonation of the methyl groups in $[Me(Ph)PN]_3$ and subsequent reaction with the simple electrophile MeI gave the anticipated ethyl derivatives,[4] thus providing precedence for similar reactions involving other electrophiles. Although reactions of the deprotonated cyclic phosphazene with $BrC(=O)CMe_2Br$ or ICH_2COOEt were considered possible methods to obtain ketone or ester derivatives, these actually facilitated a metal−halogen exchange to give the halogenated phosphazenes, **4** and **5** (eq 2). When *cis*-$[Me(Ph)PN]_3$, **2**, was treated with 3.2 equiv of *n*-BuLi in tetrahydrofuran (THF) at −78 °C, a white slurry of the lithium salt of the cyclophosphazene formed. Addition of 3.3 equiv of the halogenating reagents, EX (where EX = C_2Cl_6, $BrC(O)CMe_2Br$, or ICH_2COOEt), yielded the trihalogenated compounds **3**, **4**, and **5**, *cis*-$[Ph(XCH_2)P{=}N]_3$, in better than 70% yield.



(2)

In earlier work, we found that sequentially treating the cis isomer **2** with exactly 3 equiv of *n*-BuLi and MeI resulted in formation of both di- and trisubstituted cyclic phosphazenes.[4] However, the formation of the disubstituted product was essentially eliminated in these cases by using a slight excess of both *n*-BuLi (ca. 3.2 equiv) and C_2Cl_6, $BrC(O)CMe_2Br$ or ICH_2COOEt. Bromination was also facilitated by the reaction of the phosphazene anion with dibromoethane, but in this case a mixture of the mono-, di-, and tribrominated cyclic phosphazenes, **6**, **7**, and **4,** in a 1:2:1 ratio, respectively, was obtained (eq 3). Even when slightly more *n*-BuLi (3.5 equiv) was used to compensate for possible traces of moisture and to enhance complete deprotonation, the composition of the mixture did not change. Small amounts of the dibrominated product **7** were also found in the reaction with $BrC(O)CMe_2Br$. Attempts to brominate and chlorinate with either elemental bromine or chloroethyl acetate were unsuccessful although similar reactions have been reported on the methyl groups of N-silylphosphoranimines.[7]



(3)

All of the new compounds are air-stable, very soluble in polar solvents such as CH_2Cl_2, ethyl acetate, and THF, and slightly soluble in hexanes and ether. Although column chromatography was used to separate the bromo derivatives, the chloro and iodo derivatives needed only short column/frit filtration for purification. Crystals of each compound were grown in ethyl acetate or dichloromethane.

The ^1H, ^{31}P, and $^{13}C\{^1H\}$ NMR spectra for **3**, **4**, and **5** were very simple as consistent with the symmetrical cis geometry. The ^{31}P NMR spectra showed only one signal at δ 17.4, 16.5, and 17.4, respectively. These are upfield from the simple alkyl compounds, *cis*-$[Et(Ph)P{=}N]_3$ (δ 24.5)[4] and *cis*-$[Me(Ph)P{=}N]_3$ (δ 19.6).[2] In the ^1H NMR spectra for **3**, **4**, and **5**, the methylene proton chemical shifts are between δ 3.5 and 3.8, which is considerably downfield from the P−C−H signals in the simple alkyl compounds,[2,4] because of the electron-withdrawing effect of the electronegative halogen atoms. The P−H coupling constants of ca. 6−7 Hz are smaller than typical P(V) coupling constants of 12−14 Hz. Similar coupling constants have also been observed for haloalkyl phosphoranimines, $Me_3SiNP(OCH_2CF_3)(CH_2Br)$-Me.[7] The only other notable feature in the spectra is the upfield signal at δ 4.4 in the ^{13}C NMR spectrum for the methylene carbons in the iodo compound **5**. This correlates with the slightly upfield shift of the methylene protons in the ^1H NMR spectrum of **5** relative to the methylene protons in compounds **3** and **4**. This is a typical trend for NMR spectra of halogenated compounds.[8]

The NMR spectra for the mono- and dibrominated compounds, **6** and **7**, were somewhat more complex. The ^{31}P NMR spectrum clearly showed distinct signals for the two different types of phosphorus atoms in **6** at δ 14.8 and 21.1 with a relative intensity of 1:2, whereas the spectrum of **7** also contained two signals at δ 15.5 and 22.1 with a

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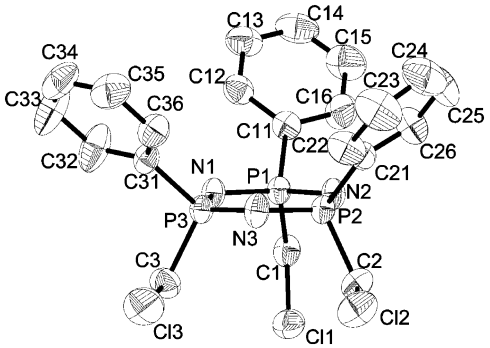

Figure 1. Thermal ellipsoid plot of **3**, *cis*-$[Ph_3(ClCH_2)_3P_3N_3]$ (40% probability ellipsoids for non-hydrogen atoms are shown).

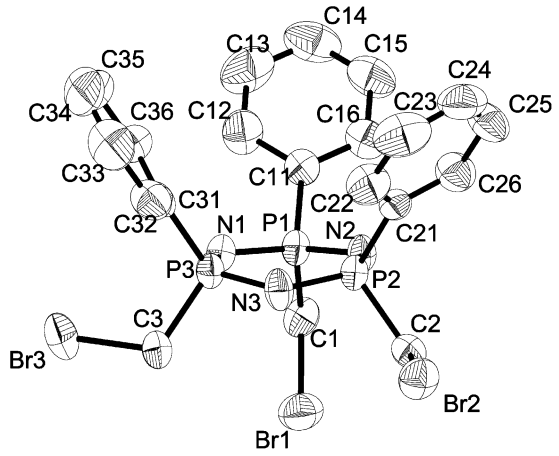

Figure 2. Thermal ellipsoid plot of **4**·CH_2Cl_2, *cis*-$[Ph_3(BrCH_2)_3P_3N_3]$ (40% probability ellipsoids for non-hydrogen atoms; lattice solvent not shown).

relative intensity of 2:1. The signals at δ 21 and 22 are in the same region as the phosphorus resonance in the parent cyclic phosphazene, **2**, and clearly correspond to the unsubstituted *P*CH_3 resonance. The signals at ca. δ 15 correspond to the phosphorus atoms attached to the derivatized CH_2Br groups and are in the same range as the single signal observed for the fully brominated compound **4**. The ^{31}P NMR signals for the *P*CH_2Br phosphorus atoms increased slightly across the mono-, di-, and tribromo series (i.e., δ 14.8, 15.5, and 16.5, respectively), reflecting the increased deshielding effect of increased numbers of bromine atoms. In addition to two different kinds of aromatic resonances, the ^{1}H NMR spectrum for the monosubstituted derivative **6** contained one doublet for the CH_3 protons at 1.89 (J_{PH} = 14.2 Hz) and one multiplet arising from the methylene group at δ 3.49 with an intensity ratio of 3:1, respectively. Similarly, the ^{1}H NMR spectrum of **7** also clearly showed a methyl doublet (δ 1.93, J_{PH} = 14.3 Hz) and a methylene multiplet (δ 3.59). Finally, the proton decoupled ^{13}C NMR spectra for **6** and **7** also contained doublets for both the methylene (**6**, δ 33.0, J_{PC} = 93.9 Hz; **7**, δ, 31.7, J_{PC} = 97.4 Hz) and the unsubstituted methyl groups (**6**, δ 23.9, J_{PC} = 101.7 Hz; **7**, δ 24.0, J_{PC} = 100.6 Hz). Strong absorptions for the P=N stretching frequency were observed in the IR spectra of each of the new compounds, **3**−**7**, and all of the spectroscopic data are consistent with the solid-state structures discussed below.

The crystal structures of **3**−**7** were determined and are shown in Figures 1−5. The crystal data are presented in

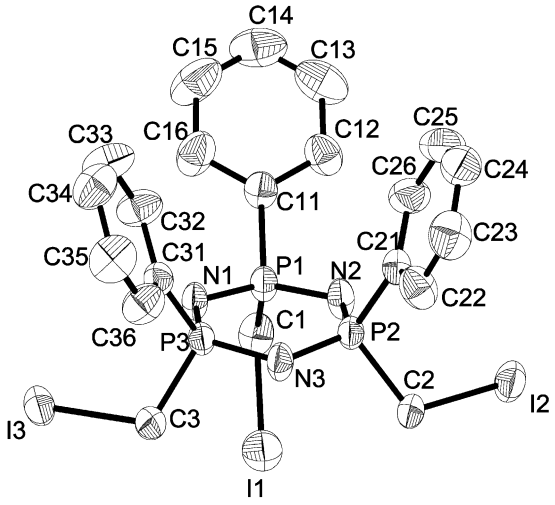

Figure 3. Thermal ellipsoid plot of **5**, *cis*-$[Ph_3(ICH_2)_3P_3N_3]$ (40% probability ellipsoids for non-hydrogen atoms are shown).

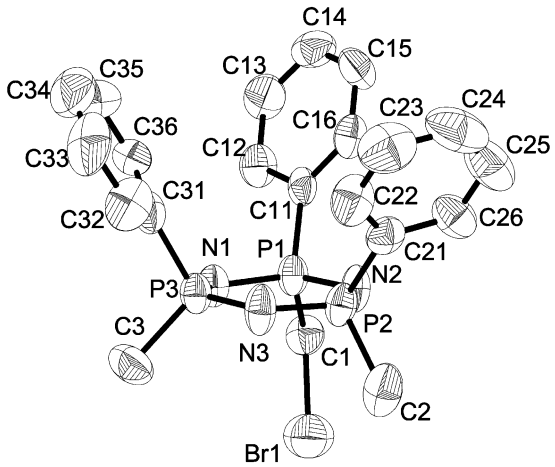

Figure 4. Thermal ellipsoid plot of **6**, *cis*-$[Ph_3(BrCH_2)(CH_3)_2P_3N_3]$ (40% probability ellipsoids for non-hydrogen atoms).

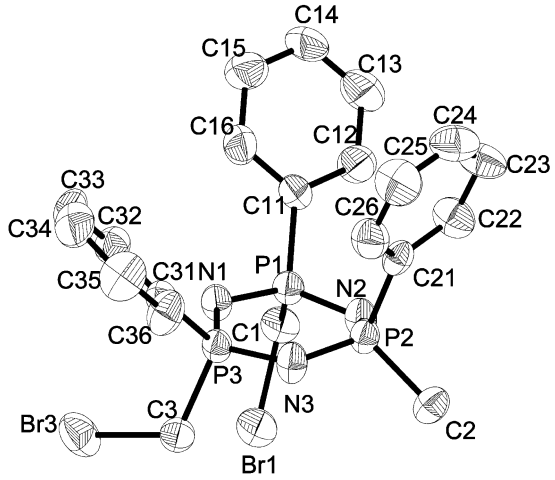

Figure 5. Thermal ellipsoid plot of **7**, *cis*-$[Ph_3(BrCH_2)_2(CH_3)P_3N_3]$ (40% probability ellipsoids for non-hydrogen atoms).

Table 1, and selected bond distances and angles are given in Table 2. All of the compounds possess cis geometries with three phenyl rings on one side of the P_3N_3 ring and methyl or haloalkyl groups on the other side. The molecules of **3** are connected by intermolecular hydrogen bonding between

Table 1. Crystal Data[a] and Structure Refinement for **3**−**8**

compound	**3**	**4**·CH_2Cl_2	**5**	**6**	**7**	**8**
empirical formula	$C_{21}H_{21}Cl_3N_3P_3$	$C_{21}H_{21}Br_3N_3P_3$·$^1/_2CH_2Cl_2$	$C_{21}H_{21}I_3N_3P_3$	$C_{21}H_{23}BrN_3P_3$	$C_{21}H_{22}Br_2N_3P_3$	$C_{27}H_{30}N_3O_3P_3S_3$
formula weight	514.67	690.51	789.02	490.24	569.15	633.63
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	*P*2/*c*	*C*2/*c*	$P\bar{1}$	*P*21/*c*	*P*21/*c*	$P\bar{1}$
a, Å	12.278(1)	16.4817(9)	8.9013(5)	8.867(1)	10.9206(6)	11.389(1)
b, Å	9.287(1)	15.4102(9)	11.3382(7)	12.671(1)	12.6846(9)	11.623(1)
c, Å	21.823(2)	20.9980(13)	14.5494(10)	20.352(2)	17.7519(16)	14.291(1)
α, deg			74.881(4)			101.409(4)
β, deg	104.413(6)	96.699(5)	73.207(5)	92.183(9)	105.310(7)	101.971(5)
γ, deg			71.698(4)			118.379(4)
V, Å^3	2410.1(4)	5296.8(5)	1311.1(1)	2285.0(4)	2371.8(3)	1528.6(2)
Z	4	8	2	4	4	2
ρ_{cald}, (g cm^{-1})	1.418	1.731	1.999	1.425	1.594	1.377
μ, mm^{-1}	0.594	4.867	3.773	2.021	3.633	0.433
extinction coefficient[15]	0.0015(5)	0.00037(9)	0.0091(6)	0.0012(9)	0.0015(4)	0.0221(19)
R1 [$I > 2\sigma(I)$][b]	0.038	0.057	0.032	0.074	0.050	0.035
wR2[all data][b]	0.100	0.138	0.086	0.186	0.113	0.099

[a] Graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + F_o^2]/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**−**8**

	3	**4**	**5**	**6**	**7**	**8**
			Bond Lengths			
P(1)−N(1)	1.599(2)	1.586(5)	1.592(4)	1.602(6)	1.599(4)	1.5962(18)
P(1)−N(2)	1.599(2)	1.591(6)	1.587(4)	1.591(6)	1.599(4)	1.5975(18)
P(2)−N(2)	1.602(2)	1.604(6)	1.594(4)	1.590(6)	1.600(4)	1.6015(17)
P(2)−N(3)	1.590(2)	1.580(5)	1.602(4)	1.601(6)	1.604(4)	1.5910(17)
P(3)−N(3)	1.585(2)	1.618(6)	1.605(4)	1.589(6)	1.598(4)	1.5968(17)
P(3)−N(1)	1.604(2)	1.589(6)	1.593(4)	1.598(6)	1.596(4)	1.5993(18)
P(1)−C(1)	1.813(3)	1.807(7)	1.809(5)	1.828(7)	1.808(5)	1.799(2)
P(2)−C(2)	1.815(3)	1.812(7)	1.805(5)	1.805(5)	1.792(5)	1.818(2)
P(3)−C(3)	1.814(3)	1.795(7)	1.797(5)	1.808(5)	1.798(5)	1.814(2)
P(1)−C(11)	1.799(3)	1.801(7)	1.796(5)	1.809(7)	1.794(5)	1.799(2)
P(2)−C(21)	1.794(12)[a]	1.800(7)	1.802(5)	1.801(5)	1.813(6)	1.800(2)
P(3)−C(31)	1.797(2)	1.799(8)	1.804(5)	1.805(5)	1.804(5)	1.797(2)
C(1)−X(1)[c]	1.785(3)	1.942(7)	2.124(5)	1.926(7)	1.927(5)	1.793(2)
C(2)−X(2)	1.771(3)	1.922(7)	2.136(4)			1.796(2)
C(3)−X(3)	1.771(3)	1.939(7)	2.136(5)		1.939(5)	1.799(2)
			Bond Angles			
N(1)−P(1)−N(2)	118.1(1)	117.6(3)	118.4(2)	118.1(3)	117.4(2)	118.22(9)
N(2)−P(2)−N(3)	117.8(1)	117.9(3)	117.0(2)	117.6(3)	116.4(2)	117.81(9)
N(3)−P(3)−N(1)	117.5(1)	117.1(3)	117.6(2)	117.3(3)	118.1(2)	117.67(9)
P(1)−N(1)−P(3)	121.5(1)	122.6(4)	121.7(2)	121.1(4)	121.5(3)	121.60(11)
P(2)−N(2)−P(1)	121.1(1)	121.9(3)	122.2(2)	122.0(4)	119.8(3)	121.58(11)
P(3)−N(3)−P(2)	122.1(1)	121.0(4)	121.3(2)	122.4(4)	120.6(3)	121.42(11)
C(1)−P(1)−C(11)	99.9(1)	102.0(3)	101.2(2)	101.5(3)	101.0(2)	100.61(10)
C(2)−P(2)−C(21)	104.6(5)[b]	103.8(3)	105.1(2)	107.0(4)	104.2(3)	106.15(10)
C(3)−P(3)−C(31)	104.3(1)	105.4(3)	105.5(2)	103.7(3)	105.3(3)	104.84(10)

[a] Average of 1.827(10) and 1.760(14). [b] Average of 107.7(4) and 101.4(5). [c] X = Cl (**3**), Br (**4, 6, 7**), I (**5**), S (**8**).

a methylene hydrogen and a halogen atom, as shown in Figure 6. The C···X distances are 3.746(8) Å, and the apparent C−H−X angle is 155.1(2)°. The orientation of the halogen atoms with respect to the P_3N_3 plane is distinctly different for each of the trisubsituted cyclic phosphazenes. In each case, one halogen (X(1)) lies beneath the PN ring, but the location of the other two are significantly different in each of the three structures. This is noted by the abbreviated ellipsoid plots (Figure 7) in which the phenyl rings are omitted. In compound **3**, the torsion angles N(3)−P(1)−C(1)−Cl(1), N(3)−P(1)−C(2)−Cl(2), and N(3)−P(1)−C(3)−Cl(3) are −6.4(2)°, 5.3(2)°, and −4.9(2)°, respectively, but in compound **5**, the torsion angles N(3)−P(1)−C(1)−I(1), N(3)−P(1)−C(2)−I(2), and N(3)−P(1)−C(3) −I(3) are −1.4(3)°, −154.7(2)°, and 151.5(3)°, respectively. In contrast to above, the least symmetrical arrangement was observed for the bromo analogue **4**, where the torsion angles N(3)−P(1)−C(1)−Br(1), N(3)−P(1)−C(2)−Br(2), and N(3)−P(1)−C(3)−Br(3) are −2.9(5)°, −7.0(4)°, and 147.4(3)°, respectively.

All P−N bond distances (mean 1.597(7), 1.595(14), 1.596(7), 1.595(6), and 1.599(3) Å for **3**, **4**, **5**, **6**, and **7**, respectively) are similar to *cis*-[Me(Ph)P═N]$_3$,[2] *cis*-[Et(Ph)P═N]$_3$,[4] (Me$_2$P═N)$_3$,[9] and (Ph$_2$P═N)$_3$[10] and other cyclophosphazenes that do not contain P−C bonded substituents.[11] The P−aryl distances for **3** (mean 1.797(3) Å), **4**

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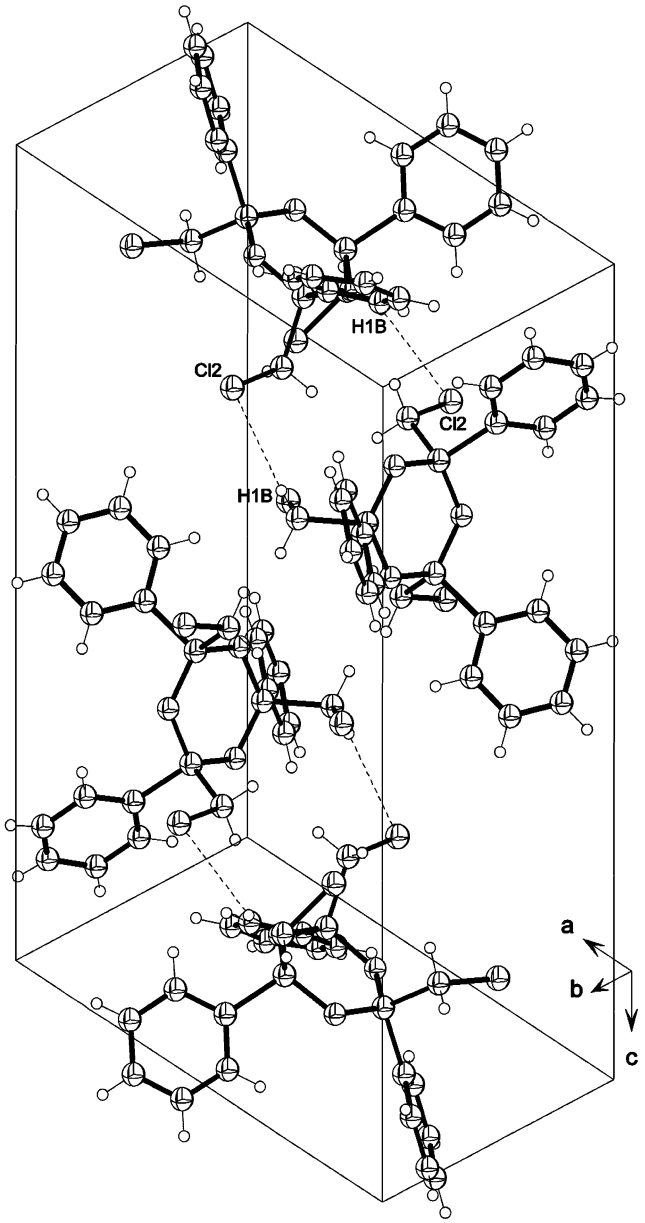


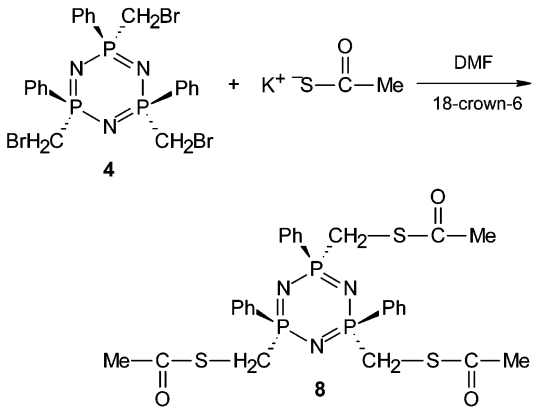
Figure 6. The crystal packing diagram of **3** and hydrogen bonding in the unit cell.

(mean 1.800(1) Å), **5** (mean 1.801(1) Å), **6** (mean 1.805(4)), and **7** (mean 1.804(9)) and the P−alkyl distances for **3** (mean 1.814(1) Å), **4** (mean 1.805(9) Å), **5** (mean 1.804(7) Å), and **7** (mean 1.799(8) Å) are also very similar to typical P−aryl and P−alkyl distances of reported phosphazenes.[2,4,9,10] The unique P(1)−C(1) bond distance in **6**, however, is somewhat longer (1.828(7) Å) presumably because of the electronic effect of the lone bromine atom attached to C(1). The mean values of P−N−P (between 120° and 121°) and N−P−N (117.3° and 117.8°) angles for **3**−**7** are in the range of typical cyclophosphazenes. The exocyclic R−P−R angles in **3**−**7** reflect the position of the halogen atoms with respect to the P_3N_3 rings. The C(1)−P(1)−C(11) angles (99.9(1)°, 102.0(3)°, 101.2(2)°, 101.5(3)°, and 101.0(2)° for **3**, **4**, **5**, **6**, and **7**, respectively) are significantly smaller than the other C−P−C angles that range between 103.7° and 107.0°. The smaller angle corresponds to the PCH_2X group that wraps under the P_3N_3 ring. The steric effect of the phosphazene ring thus decreases the alkyl−P−aryl angle. Finally, the P_3N_3 rings are planar to within ±0.05, 0.06 , 0.06, 0.05, and 0.11 Å for **3**, **4**, **5**, **6**, and **7**, respectively, and the phosphazene rings have a slight chair and boat form for **3** and **4** and a puckered form for **5**, **6**, and **7**, because of intra- and intermolecular steric effects as observed for $(PhRPN)_3$ (R = Me or Et)[2,4] and slight steric repulsion of the phenyl groups.

Thermal Properties. Differential scanning calorimetry (DSC) was used to determine the thermal transitions of the new trimers, **3**−**7**. Endothermic peaks corresponding to melting points (T_m) (Table 3) were generally higher than the T_m for **2** (157 °C), as predicted with the incorporation of the larger halogen atoms. For similar reasons, the T_m of the trisubstituted cis isomer **4** is higher than the T_m of mono- or disubstituted isomers, **6** and **7**. The highest T_m was observed for **3,** the derivative with the most electronegative chloroalkyl group. No evidence for thermal polymerization was observed, but broad endothermic curves between 300 and 320 °C are likely because of sublimation.

The thermogravimetric analyses (TGA) data for **3**−**7** were all similar, with each showing a one-step weight loss beginning at ca. 250 or 300 °C with less than 70% weight loss at 400 °C (Table 3). These new haloalkyl cyclophosphazenes appear to have greater thermal stability than the cis isomers of either $[Me(Ph)PN]_3$ or $[Et(Ph)PN]_3$, where the weight loss at 350 °C exceeded 90%. The mono- and dibromo compounds were slightly less thermally stable than the trisubstituted compounds.

Reactions with Nucleophiles. One of the potential applications of the haloalkyl derivatives of the alkylarylphosphazenes is their use as precursors to different types of functionalized cyclophosphazenes, with the halogens serving as leaving groups in nucleophilic substitution reactions. However, numerous attempts to react the tribromo derivative **4** with sodium methoxide or sodium phenoxide failed to give the expected ether derivatives. The conditions for these attempts included refluxing in THF and heating at 60 °C in dimethylformamide (DMF) in the presence of 15-crown-5 for 12−15 h. However, when a softer nucleophile, KSC(=O)CH_3, was used along with 18-crown-6 and DMF, good yields of the trisubstituted thioester derivative, **8**, were obtained (eq 4).



(4)

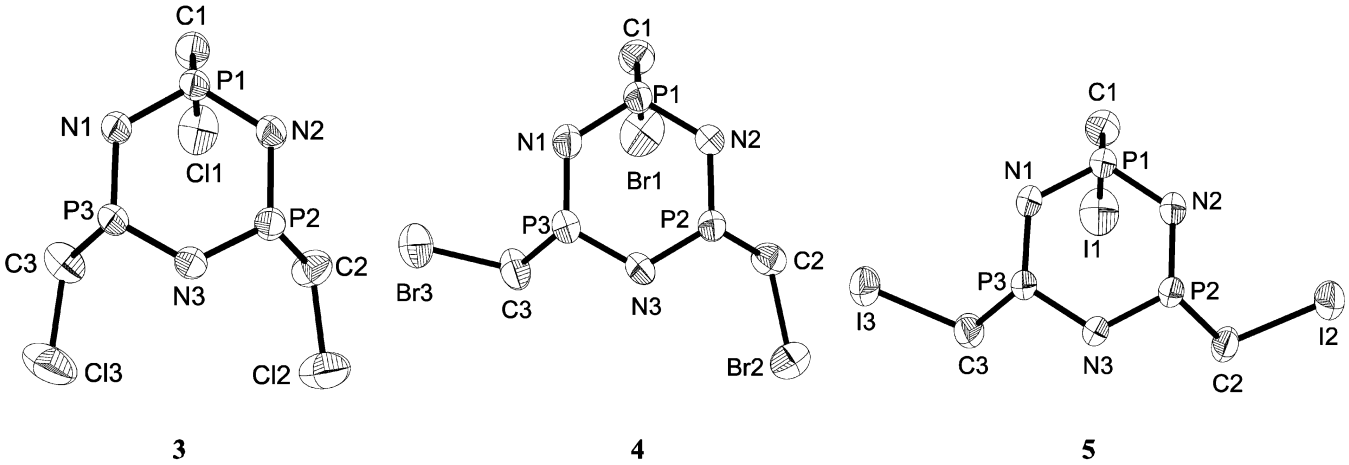


Figure 7. Abbreviated ellipsoid plots of trihalogenated cyclophosphazenes showing halogen orientation.

Table 3. DSC and TGA Data for Cyclotriphosphazenes

	DSC	TGA (% wt loss)			
trimer	T_m (°C)	250 °C	300 °C	350 °C	400 °C
1	97	5	23	92	
2	156	7	32	99	
3	198	2	3	18	54
4	185	6	16	37	50
5	184	3	4	18	43
6	155	4	16	37	65
7	163	6	20	41	57
8	133	2	18	42	72

Purification by column chromatography gave a pure sample of **8** that was characterized by NMR and IR spectroscopy and X-ray crystallography. The ^{31}P NMR spectrum contained the expected single signal at δ 19.5 and the ^{1}H and ^{13}C NMR spectra showed the typical aryl signals and a new signal for the carbon atom adjacent to the carbonyl group. The characteristic carbonyl signal at δ 194 was also clearly observed in the ^{13}C NMR spectrum. The melting point of **8** at 133 °C was significantly lower than the precursor bromo compound **4**, presumably due to the increased length of the new substituents which decrease the order in the solid state. TGA data for the thioester **8** showed a one-step weight loss similar to that of compounds **2**−**7**. Attempts to cleave the sulfur−acetate bond using strongly basic conditions gave unidentifiable mixtures rather than the desired thiol derivatives.

The crystal structure (Figure 8) and data (Tables 1 and 2) clearly show the cis geometry of the new thioester derivative, **8**. The sulfur atoms, however, do not assume positions similar to that of the bromine in the parent compound **4**. Instead, their arrangement with respect to each other is more like that of the trichloro compound **3** with torsional angles of −0.9(2)°, 27.6(2)°, and −4.2(2)° for N(3)−P(1)−C(1)−S(1), N(3)−P(1)−C(2)−S(2), and N(3)−P(1)−C(3)−S(3), respectively. The $CH_3C(=O)$ groups are staggered, presumably minimizing steric repulsions.

The P−N and P−C bond distances (means P−N, 1.597(4); P−aryl, 1.799(2); and P−alkyl, 1.810(10) Å) are typical of these nongeminally substituted alkylaryl cyclophosphazenes. As observed for **2**−**7**, the P−N−P and the N−P−N bond angles are also similar to those of other cyclic

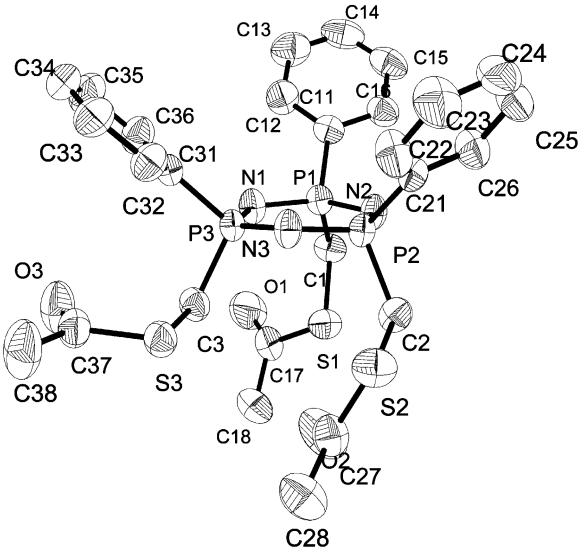


Figure 8. Thermal ellipsoid plot of **8**, cis-{Ph[$CH_3C(=O)SCH_2$]PN}$_3$ (40% probability ellipsoids for non-hydrogen atoms).

phosphazenes, and the C(1)−P(1)−C(11) bond angle of 100.61 Å is smaller than the other two C−P−C angles for the reasons discussed above. Finally, the P_3N_3 ring has a slightly puckered conformation with a deviation from planarity of ±0.05 Å.

Conclusion

A series of basket-shaped, nongeminally substituted haloalkyl-phenyl cyclophosphazenes were prepared from the cis isomer of [Me(Ph)PN]$_3$, **2**, via deprotonation of the methyl groups and treatment with halogen-containing electrophiles. In addition, the mono- and dibromoalkyl derivatives were also isolated. The new cyclic compounds had higher melting and sublimation points than those of the parent compound. Although the new bromoalkyl compounds were less reactive than simple alkylhalide analogues, RX, the electron-withdrawing effect of the phosphorus attached to the brominated carbon atom appears to favor reactions of the bromoalkyl group with softer nucleophiles. It is noted that the preparation of the haloalkyl compounds expands the methods for derivatizing the P−Me substituted alkylaryl phosphazenes. Although deprotonation to form P−CH_2Li

groups affords a site for reactions with electrophiles, the new $P-CH_2X$ groups reported here are suitable for reactions with nucleophiles, as demonstrated by the reaction with the thioacetate anion. Thus, these new haloalkyl cyclophosphazenes may be useful for the preparation of a variety of other cyclic compounds. The reactions reported here also serve as models for the analogous polymer $[Me(Ph)PN]_n$ for which the haloalkyl derivatives have not been cleanly isolated using X_2 as electrophiles.[12]

Experimental Section

Unless otherwise stated, all reactions were performed in flame-dried or oven-dried glassware by using standard Schlenk techniques. Toluene, benzene, hexanes, and dichloromethane were distilled from CaH_2; THF and diethyl ether were distilled from Na/benzophenone and stored over molecular sieves under nitrogen until they were needed. The *n*-BuLi, ICH_2COOEt, $BrC(O)CMe_2Br$, C_2Cl_6, and dibromoethane were used as received from commercial sources. Published procedures were used to prepare and isolate *cis*-[Me(Ph)P═N]$_3$, **2**,[2] and $CH_3C(═O)SK$.[13] All manipulations for the syntheses were done under an atmosphere of dry nitrogen, but the cyclic phosphazene products were handled in the atmosphere. NMR spectra were recorded on a SGI/Bruker DRX-400 spectrometer. Positive ^1H and ^{13}C NMR chemical shifts and ^{31}P NMR shifts are downfield from the external references Me_4Si and H_3PO_4, respectively. Elemental analyses and IR spectra were obtained on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106 and a Nicolet 560 IR spectrometer, respectively. Thermal data was collected on a TA Instruments SDT 2960 and DSC 2010.

X-ray Crystallography. Crystals of **3, 4**·CH_2Cl_2**, 5, 6**, and **7** were colorless, but **8** was pale-yellow. All single-crystal samples were plate-shaped. The diffraction data of all structures were collected on a Bruker P4 diffractometer at room temperature. The pertinent crystallographic data are summarized in Table 1. Final unit-cell parameters were obtained by a least-squares fit of the angles of ca. 40 accurately centered reflections in the range of $18° < 2\theta < 30°$. Data were recorded with ω scans. All structures were solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL-Plus package.[14] A phenyl ring, C(21) through C(26), in structure **3** was disordered which was refined with restraints. In the lattice of **4**, half of a CH_2Cl_2 solvent molecule was found for one phosphazene molecule. Structures were refined anisotropically on F^2 (SHELXL97).[15] Hydrogen atoms were constrained with a riding model. Selected bond distances and angles are listed in Table 2. Further details regarding the crystal data and refinement, as well as full tables of bond lengths and angles for each structure reported in this paper are presented in the Supporting Information.

Preparation of *cis*-[Ph$_3$(ClCH$_2$)$_3$P$_3$N$_3$], 3. In a typical procedure, 0.34 g (0.83 mmol) of *cis*-[Me(Ph)PN]$_3$, **2**, was placed in a two-necked, 50 mL round-bottom flask equipped with a magnetic stir bar, a nitrogen inlet adapter, and a rubber septum. Freshly distilled THF (10 mL) was added to the flask, and the solution was cooled to −78 °C. Then, 3.5 equiv of *n*-BuLi was added to the solution, and the white slurry was stirred for 4 h at that temperature. Next, 3.5 equiv of C_2Cl_6 (0.7 g) was added to the slurry at −78 °C, and this mixture was stirred at least 12 h at room temperature. The mixture was transferred to a 250-mL separatory funnel, and aqueous KOH (40 mL, 1.5 M) was added. The compounds were extracted with CH_2Cl_2 (2 × 20 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in 20 mL of ethyl acetate and then filtered through a 15 mL glass frit containing a layer of silica gel (2 cm). The volatiles were removed under vacuum to give a white solid, 0.38 g (89%). Crystallization by slow evaporation of ethyl acetate at room temperature gave the product as colorless crystals. ^1H NMR ($CDCl_3$): δ 3.79 (d, 6 H, PCH_2Cl, J_{PH} = 6.5 Hz), 7.33−7.43 (m, 9 H, C_6H_5), 7.86−7.92 (m, 6 H, C_6H_5). ^{13}C NMR{^1H} ($CDCl_3$): δ 43.5 (d, PCH_2Cl, J_{PC} = 99.6 Hz), 128.1 (d, Ph, J_{PC} = 13.2 Hz), 130.7 (d, Ph, J_{PC} = 9.9 Hz), 131.6 (d, Ph, J_{PC} = 2.8 Hz), 133.6 (d, Ph, J_{PC} = 135.4 Hz). ^{31}P NMR{^1H} ($CDCl_3$): δ 17.4. IR (KBr, neat, cm^{-1}): 3059 m, 2983 m, 2920 m, 1590 m, 1480 m, 1437 s, 1388 m, 1230 s, 1214 s, 1188 vs, 1166 vs, 1133 s, 1027 s, 884 m, 810 s, 769 m, 747 m, 701 s, 680 s, 662 m, 578 m, 521 s, 502 m, 470 m, 452m. Anal. Calcd for $C_{21}H_{21}P_3N_3Cl_3$: C, 49.01; N, 8.16; H, 4.11. Found: C, 49.53; N, 8.08; H, 4.24. Mp: 198 °C.

Preparation of *cis*-[Ph$_3$(BrCH$_2$)$_3$P$_3$N$_3$], 4, 6, and 7. In a typical procedure, 1.00 g (2.43 mmol) of *cis*-[Me(Ph)PN]$_3$, **2**, was placed in a two-necked, 50 mL round-bottom flask with a magnetic stir bar, a nitrogen inlet adapter, and a rubber septum. Freshly distilled THF (10 mL) was then added to the flask, and the mixture was cooled to −78 °C. The *n*-BuLi (3.5 equiv, 3.4 mL, 2.5 M in hexanes) was added to the solution. The white slurry was stirred for 4 h at −78 °C, and then $BrCH_2CH_2Br$ (3.5 equiv, 0.8 mL) was added. The mixture was allowed to warm to room temperature and stirred for 12 h. The resulting clear, light yellow solution was transferred to a separatory funnel with dichloromethane (30 mL), and aqueous KOH (40 mL, 1.5 M) was added to remove any HBr. The organic layer was separated, dried over Na_2SO_4, and filtered, and the volatiles were removed with a rotary evaporator. The residue was further dried at 50 °C under reduced pressure. The ^1H and ^{31}P NMR spectra indicated that the mono-, di-, and trisubstituted cis isomers were all present in a 1:2:1 ratio, respectively. The three compounds were separated by column chromatography (silica gel, 60 Å, ethyl acetate/hexanes = 1:1): **6**, 0.23 g, 15%, R_f = 0.89; **7**, 0.53 g, 37%, R_f = 0.81; **4**, 0.21 g, 17%, R_f = 0.51. Crystallization by slow evaporation of dichloromethane at room temperature gave each product as colorless crystals.

This reaction gives substantially better control when the electrophile $BrC(O)CMe_2Br$ is used in place of dibromoethane. Typically the tri-/disubstitution ratio was 80:20 with separation facilitated by column chromatography as described above. No monosubstituted compound was detected.

***cis*-[Ph$_3$(BrCH$_2$)$_3$P$_3$N$_3$], 4.** ^1H NMR ($CDCl_3$): δ 3.64 (d, 6 H, PCH_2Br, J_{PH} = 5.9 Hz), 7.32−7.42 (m, 9 H, Ph), 7.84−7.90 (m, 6 H, Ph). ^{13}C NMR{^1H} ($CDCl_3$): δ 30.7 (d, PCH_2Br, J_{PC} = 98.1 Hz), 128.1 (d, Ph, J_{PC} = 13.4 Hz), 130.7 (d, Ph, J_{PC} = 10.2 Hz), 131.5 (s, Ph), 133.8 (d, Ph, J_{PC} = 136.1 Hz). ^{31}P NMR{^1H} ($CDCl_3$): δ 16.5. IR (KBr, pellet, cm^{-1}): 3057 m, 3000 m, 2938 m, 1462 m, 1438 s, 1375 m, 1200 vs, 1153 vs, 1125 s, 1057 m, 1026 s, 999 m, 883 w, 868 w, 791 s, 729 s, 695 s, 627 w, 612 m, 570 m, 519 s. Anal. Calcd for $C_{21}H_{21}P_3N_3Br_3$: C, 38.92; N, 6.48; H, 3.27. Found: C, 39.22; N, 6.03; H, 3.45. Mp: 183 °C.

***cis*-[Ph$_3$(BrCH$_2$)(CH$_3$)$_2$P$_3$N$_3$], 6.** ^1H NMR ($CDCl_3$): δ 1.89 (d, 6 H, PCH_3, J_{PH} = 14.2 Hz), 3.49 (m, 2 H, PCH_2Br), 7.18−7.27 (m, 6 H, Ph), 7.35−7.41 (m, 3 H, Ph), 7.62−7.67 (m, 4 H, Ph), 7.83−7.89 (m, 2 H, Ph). ^{13}C NMR{^1H} ($CDCl_3$): δ 23.9 (d, PCH_3,

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J_{PC} = 101.7 Hz), 33.0 (d, PCH_2Br, J_{PC} = 93.9 Hz), 128.3 (d, Ph, J_{PC} = 13.1 Hz), 128.7 (d, Ph, J_{PC} = 12.7 Hz), 129.9 (d, Ph, J_{PC} = 11.2 Hz), 130.67 (s, Ph), 130.7 (d, Ph, J_{PC} = 9.6 Hz), 131.7 (d, Ph, J_{PC} = 2.7 Hz), 135.3 (d, Ph, J_{PC} = 133.3 Hz), 139.0 (d, Ph, J_{PC} = 124.9 Hz). ^{31}P NMR{^{1}H} ($CDCl_3$): δ 14.8, 21.1. IR (KBr, pellet, cm^{-1}): 3073 m, 3054 m, 2988 m, 2977 m, 2926 m, 2913 m, 1589 w, 1478 w, 1435 m, 1409 w, 1291 m, 1197 vs, 1163 vs, 1120 s, 1027 m, 934 m, 891 s, 817 s, 726 s, 696 s, 557 s, 517 s. Anal. Calcd for $C_{21}H_{23}P_3N_3Br$: C, 51.45; N, 8.57; H, 4.73. Found: C, 51.64; N, 8.34; H, 4.81. Mp: 155 °C.

***cis*-[Ph$_3$(BrCH$_2$)$_2$(CH$_3$)P$_3$N$_3$], 7.** ^{1}H NMR ($CDCl_3$): δ 1.93 (d, 3 H, PCH_3, J_{PH} = 14.3 Hz), 3.59 (m, 4 H, PCH_2Br), 7.25−7.41 (m, 9 H, Ph), 7.69−7.75 (m, 2 H, Ph), 7.82−7.87 (m, 4 H, Ph). ^{13}C NMR{^{1}H} ($CDCl_3$): δ 24.0 (d, PCH_3, J_{PC} = 100.6 Hz), 31.7 (d, PCH_2Br, J_{PC} = 97.4 Hz), 128.4 (d, Ph, J_{PC} = 12.8 Hz), 128.5 (d, Ph, J_{PC} = 13.1 Hz), 129.9 (d, Ph, J_{PC} = 10.4 Hz), 130.9 (d, Ph, J_{PC} = 2.9 Hz), 131.0 (d, Ph, J_{PC} = 10.1 Hz), 131.7 (d, Ph, J_{PC} = 2.6 Hz), 134.8 (d, Ph, J_{PC} = 134.6 Hz), 138.6 (d, Ph, J_{PC} = 126.6 Hz). ^{31}P NMR{^{1}H} ($CDCl_3$): δ 15.5, 22.1. IR (KBr, pellet, cm^{-1}): 3054 m, 2987 m, 2919 m, 1435 m, 1407 w, 1379 w, 1295 m, 1200 vs, 1159 vs, 1121 s, 1027 m, 998 m, 916 m, 895 m, 877 m, 822 m, 795 s, 729 s, 694 s, 609 m, 562 s, 520 s. Anal. Calcd for $C_{21}H_{22}P_3N_3Br_2$: C, 44.32; N, 7.38; H, 3.90. Found: C, 44.57; N, 7.22; H, 3.87. Mp: 163 °C.

Preparation of *cis*-[Ph$_3$(ICH$_2$)$_3$P$_3$N$_3$], 5. The trianion was generated as described above using 0.33 g (0.8 mmol) of *cis*-[Me(Ph)PN]$_3$, **2**, freshly distilled THF (10 mL), and TMEDA (0.4 mL). This was treated with ICH_2COOEt (0.3 mL, 3.0 equiv) at −78 °C and stirred for 12 h at room temperature, and then the volatiles were removed under vacuum. The residue was dissolved in 20 mL of toluene, and this mixture was filtered using a glass frit with a layer of Celite. The volatiles were removed from the filtrate under vacuum to give 0.4 g of a pale-yellow solid. The compound was purified by recrystallization from ethyl acetate. The first crop gave 0.28 g (44%); the second crop gave 0.08 g (13%). ^{1}H NMR ($CDCl_3$): δ 3.54 (d, 6 H, PCH_2I, J_{PH} = 7.2 Hz), 7.29−7.35 (m, 9 H, Ph), 7.83−7.88 (m, 6 H, Ph). ^{13}C NMR{^{1}H} ($CDCl_3$): δ 4.4 (d, PCH_2I, J_{PC} = 96.6 Hz), 127.7 (d, Ph, J_{PC} = 13.6 Hz), 130.4 (d, Ph, J_{PC} = 10.5 Hz), 131.0 (s, Ph), 133.6 (d, Ph, J_{PC} = 135.0 Hz). ^{31}P NMR{^{1}H} ($CDCl_3$): δ 17.4. IR (KBr, neat, cm^{-1}): 3052 m, 2991 m, 2931 m, 1966 m, 1895 m, 1820 m, 1589 m, 1479 m, 1437 s, 1376 m, 1365 s, 1199 vs, 1021 vs, 1071 s, 1042 m, 1025 s, 998 m, 876 m, 859 s, 796 m, 778 s, 768 s, 735 s, 722 s, 695 s. Anal. Calcd for $C_{21}H_{21}P_3N_3I_3$: C, 31.97; N, 5.33; H, 2.68. Found: C, 32.36; N, 5.41; H, 2.63. Mp: 184 °C.

Preparation of *cis*-{[CH$_3$C(=O)SCH$_2$](Ph)PN}$_3$, 8. A 1.00 g (1.54 mmol) sample of *cis*-[Ph ($BrCH_2$)PN]$_3$, **5**, was placed in a two-neck, 50 mL round-bottom flask equipped with a magnetic stir bar, a nitrogen inlet adapter, and a rubber septum. Dry DMF (10 mL) was added to the flask, and the mixture was stirred at room temperature. Then, 18-crown-6 (0.7 g, 6.16 mmol) and $CH_3C(=O)SK$ (1.05 g, 9.24 mmol) were added under nitrogen. The resulting dark-yellow solution was stirred at room temperature for 2 days. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and washed with water (3 × 50 mL) to remove the unreacted potassium thioacetate. The organic layer was separated, and the solvents were removed using a rotary evaporator. The oily residue was further dried at 50 °C in a vacuum oven for 1 day. The mixture was purified and separated by column chromatography (silica gel, 60 Å, columns (25 mm × 250 mm, ethyl acetate/hexanes = 1:1). The product, **8**, was recrystallized from benzene/hexane (1:2): 0.480 g, 76%, R_f = 0.55. ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 9H, CH_3S), 3.51 (d, J_{PH} = 10.0 Hz, 6H, PCH_2), 7.31−7.36 (m, 9 H, C_6H_5), 7.79−7.84 (m, 6 H, C_6H_5). ^{13}C NMR {^{1}H} ($CDCl_3$): δ 30.6 (s, CH_3), 33.1 (d, PCH_2, J_{PC} = 97.1 Hz), 128.3 (d, C_6H_5, d, J_{PC} = 13.1 Hz), 130.6 (d, C_6H_5, J_{PC} = 10.1 Hz), 131.5 (d, C_6H_5, J_{PC} = 2.4 Hz), 135.3 (d, C_6H_5, J_{PC} = 132.0 Hz), 194.0 (d, C=O, J_{PC} = 4.0 Hz). ^{31}P NMR{^{1}H} ($CDCl_3$): δ 19.5. IR (KBr, neat, cm^{-1}): 3675 m, 3065 m, 2954 m, 2900 s, 1701 s, 1686 s, 1437 s, 1357 s, 1198 s, 1164 s, 1130 s, 1099 s, 1069 m, 1027 m, 964 s, 873 m, 796 s, 780 m, 621 s, 528 s. Anal. Calcd for $C_{27}H_{30}N_3O_3P_3S_3$: C, 51.18; N, 6.63; H, 4.77. Found: C, 51.15; N, 6.42; H, 4.79. Mp: 133 °C.

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Supporting Information Available: X-ray crystallographic files in CIF format for **3**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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