Reactions of Alkali-metal Azides with Some Halogenophosphorus Compounds

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The reactions of alkali-metal (Li or Na) azides with PCl_3, PBr_3, PI_3, $[PCl_4][SbCl_6]$, and $[N(n\text{-}C_5H_{11})_4][PCl_6]$ in solution in suitable organic solvents have been investigated by means of ^{31}P n.m.r. spectroscopy. Both substitution and decomposition (with loss of N_2) reactions have been observed; the decomposition products are polymeric cyclic or acyclic phosphazenes, depending on the starting material. This has been confirmed for the cyclic trimers and tetramers by direct substitution of azide into $(NPCl_2)_3$, $(NPCl_2)_4$, and their bromo-analogues. For the six-co-ordinate anions $[PCl_{6-n}(N_3)_n]^-$ $(2 \leqslant n \leqslant 4)$, where isomerism is possible, one isomer appears to form preferentially in each instance. Structural assignments have been made on the basis of pairwise interactions. Isolation of the products has not in general been attempted because of the hazards involved.

THERE are many examples of the replacement of halogeno-groups in phosphorus compounds by pseudohalogens such as cyanate, thiocyanate, and cyanide, and the reactions may often be conveniently followed by means of ^{31}P n.m.r. spectroscopy.[1,2] Comparatively few azido-derivatives have been reported without an organo-group present,[3] although the fully substituted species $P(N_3)_3$,[4] $P(N_3)_3O$,[4,5] $[P(N_3)_4]^+$,[6,7] and $[P(N_3)_6]^-$[8,9] are known. In some instances, reactions have been described which may well have proceeded *via* halogeno-azido-intermediates, even though these were not identified. The reaction of excess of PBr_3 with sodium azide at 438—440 K thus gave a mixture of $(NPBr_2)_n$ polymers,[10] while the photolytic reaction of HN_3 with PCl_3 between 195 and 206 K yielded a tetrameric product of composition $(N_8P_5Cl_9)_4$;[11] $PCl_2(N_3)$ was postulated as an intermediate in the latter case, but direct evidence for this was lacking. Very recently we described in a preliminary communication [3] the identification by means of ^{31}P n.m.r. spectroscopy of the compounds $PX_n(N_3)_{3-n}$, $PX_n(N_3)_{3-n}S$, and $PBr_n(N_3)_{3-n}O$, where X = Cl or Br and $0 \leqslant n \leqslant 3$, formed by addition of sodium azide to the appropriate phosphorus halide in acetonitrile solution. The results of further investigations into the species $PX_n(N_3)_{3-n}$ (X = Cl, Br, or I; $0 \leqslant n < 3$), $[PCl_n(N_3)_{4-n}]^+$ $(0 \leqslant n < 4)$, and $[PCl_n(N_3)_{6-n}]^-$ $(0 \leqslant n < 6)$, together with their decomposition products, are now reported.

EXPERIMENTAL

All manipulations, including n.m.r. sample preparation, were carried out under an inert atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, generally without further purification except for tetra-n-pentylammonium chloride, which was thoroughly dried by heating to 373 K under vacuum for 5 h. Lithium azide was prepared by the method of Hoffman-Bang.[12] The mixture of phosphonitrilic bromides was obtained according to the procedure given by Bode,[13] but the separation of trimer, tetramer, and higher polymers was not carried out. The compound $[PCl_4][SbCl_6]$ was prepared as described previously.[14] Tetra-n-pentylammonium hexachlorophosphate was obtained from the reaction of equimolar portions of $[N(n\text{-}C_5H_{11})_4]Cl$ and phosphorus(v) chloride in CH_2Cl_2 as solvent. The salt was isolated by removing the solvent *in vacuo*.

The usual procedure for preparation of n.m.r. samples was to dissolve the phosphorus compound, if solid, in the minimum quantity of solvent, and add the requisite amount of the alkali-metal azide directly to the n.m.r. sample tube. In this way the signal intensities would be maximised. The compounds PCl_3 and PBr_3 were similarly mixed with the required solvent, to give solutions for which the signals were readily visible after a single pulse. After each experiment, solutions containing azide residues were treated with an aqueous solution of sodium nitrite and acetic acid to destroy the azido-species.

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on the Fourier-transform spectrometer as indicated previously,[15] using sample tubes (outside diameter 8.4 mm). Chemical shifts were measured relative to external H_3PO_4, and are quoted with the upfield direction taken as positive. Infrared spectra were recorded on a Perkin-Elmer 457 instrument, either as contact films on CsI plates, protected by Polythene discs where necessary, or as solutions in the appropriate solvent.

RESULTS AND DISCUSSION

(*a*) $PX_n(N_3)_{3-n}$ *Systems and Their Decomposition Products*.—As previously reported,[3] PCl_3 and PBr_3 react with sodium azide in MeCN solution to give substituted species. In other solvents such as CS_2, CH_2Cl_2, and $PhNO_2$, little reaction if any was observed with sodium azide, but lithium azide proved to be effective in carrying out substitution in these media also. Some variation in shift with solvent was found, as shown in Table 1. In particular, the values for the azido-substituted species occur at somewhat higher field in CS_2, possibly reflecting specific solute–solvent interactions since the differences are larger than expected for magnetic susceptibility variations alone. The shift [5] of 16.0 p.p.m. for $P(N_3)_3$ is clearly in error, and arises from the main decomposition product, as discussed below.

Phosphorus triazide, whether derived from PCl_3 or PBr_3, decomposed rapidly in all solvents, with loss of N_2; the decomposition products gave a strong ^{31}P n.m.r. signal at 16.2 p.p.m., together with a smaller resonance at 6.5 p.p.m. The products, as expected, thus appear not to contain Cl or Br. The decomposition of $PCl_2(N_3)$, prepared by adding a small amount of $Li[N_3]$ to a large excess of PCl_3, was also studied. The ^{31}P n.m.r. spectrum of the decomposition products was identical to that obtained from PN_9, although a substantially longer time (up to several weeks) was required for complete reaction. The compound $PCl(N_3)_2$ could not be obtained in the absence of other azido-species, so its decomposition could not be studied independently. A mixture containing all three azido-derivatives gave the same ^{31}P spectrum on decomposition, however, as that described for PN_9 and $PCl_2(N_3)$.

Previous work on the decomposition of compounds of the type $PR_2(N_3)$, where $R = CF_3$,[16,17] C_3F_7,[17] or C_6H_5,[18] which often required elevated temperatures, has shown that the reaction products are phosphonitrilic polymers $(NPR_2)_n$. The compound $P(CF_3)Me(N_3)$ similarly yielded $[NP(CF_3)Me]_n$ on decomposition,[17] while reaction of $PPhCl_2$ with $SiPh_3(N_3)$ or $SiMe_3(N_3)$ produced $[NP(C_6H_5)Cl]_n$,[19] and the action of sodium azide on a PPh_2Cl–$PPhCl_2$ mixture led to isolation of the tetramer $N_4P_4Ph_6Cl_2$.[20] Similarly, photolysis of HN_3 with PCl_3 gave a mixture of phosphonitrilic polymers containing some azide ligands,[11] and the ^{31}P n.m.r. spectrum of the major product is identical with that described above. It is thus reasonable to assume that phosphorus(III) chloroazides decompose to give phosphonitrilic polymers. The chemical shifts indicate that either linear species or cyclic compounds $(NPX_2)_n$, $[NPX(N_3)]_n$, or $[NP(N_3)_2]_n$ with $n \geq 5$ are formed,[1] as confirmed by the data for azide substitution into $(NPCl_2)_3$ and $(NPCl_2)_4$, discussed below. The most probable product from the relative peak intensities is a linear polymer with $n > 4$, where the resonance at 16.2 p.p.m. arises from middle groups and the smaller signal at 6.5 p.p.m. from end groups in the polymer chain. Although P–P coupling, through nitrogen, could occur between inequivalent phosphorus atoms in a linear polymer, this effect was not observed. The coupling constants in phosphazenes are not large,[1] however, and the effect of coupling could well be obscured by line broadening, due either to exchange or to the presence of polymers of differing chain length with slightly different but unresolvable chemical shifts. The results also suggest that the extent of azide substitution has little, if any, effect on the chemical shift. This is analogous to the PCl_3O–$P(N_3)_3O$ system, where the overall shift difference is less than 3 p.p.m.,[1,3-5] and is in agreement with the trend of smaller shift differences on substitution with increasing polymer size. The shift difference caused by N_3,Cl substitution falls markedly from $(NPCl_2)_3$ (9.7 p.p.m.) to $(NPCl_2)_4$ (3.8 p.p.m.), as shown by Table 2, and although direct evidence is lacking this trend is expected to continue for higher polymers. In chlorophosphazenes the position in the ring or chain has very little effect on the shift beyond $(NPCl_2)_4$; the values reported for $(NPCl_2)_5$ to $(NPCl_2)_8$ are all in the range 17 ± 1 p.p.m., and do not follow a regular sequence.[1] These values are very close to the shift of 16.2 p.p.m. assigned above to middle groups. It is clear from our results that the fully azido-substituted decomposition product gives shifts of 6.5 and 16.2 p.p.m., since an identical ^{31}P n.m.r. spectrum results on decomposition of $P(N_3)_3$ prepared from either PCl_3 or PBr_3. (This conclusion is also supported by complete azide substitution into the higher cyclic bromophosphazene polymer, which gives rise to a single peak at 16.2 p.p.m., as discussed in the following section.)

TABLE 1

Effect of solvent on $\delta(^{31}P)$ for $PX_{3-n}(N_3)_n$ (X = Cl or Br)

	$\delta(^{31}P)$/p.p.m. for $PCl_{3-n}(N_3)_n$				$\delta(^{31}P)$/p.p.m. for $PBr_{3-n}(N_3)_n$			
Solvent	PCl_3	$PCl_2(N_3)$	$PCl(N_3)_2$	$P(N_3)_3$	PBr_3	$PBr_2(N_3)$	$PBr(N_3)_2$	$P(N_3)_3$
CH_2Cl_2	−219.6	−161.6	−144.6	−130.2	−228.9	−169.3	−158.0	
$PhNO_2$	−220.8	−162.1	−145.7	−131.2	−228.2	−168.6	−155.2	
CS_2	−219.3	−160.4	−143.3		−227.3	−167.8	−150.2	−126.9
MeCN	−220.6	−164.4	−149.1	−134.6	−230.1	−170.0	−157.1	−134.6

The decomposition product from $P(N_3)_3$, expected to be $[NP(N_3)_2]_n$, was isolated as a viscous, creamy, explosive oil. Its i.r. spectrum as a contact film showed a strong, broad band at 2 150 cm^{-1}, and a similar strong band was seen at 2 165 cm^{-1} in MeCN solution, ascribed to $\nu_{asym}(N_3)$.[21,22] **CAUTION.** A sample submitted for nitrogen analysis exploded, and no estimation of the nitrogen content could be obtained. The phosphorus content was determined by the normal method [14] as 22.6% $\{[NP(N_3)_2]_n$ requires 24.0%$\}$. The experimental result is in even closer agreement with that for a linear fully azido-substituted polymer when the end groups are taken into account.

The expected decomposition product of $PCl_2(N_3)$ is $(NPCl_2)_n$, with no azide groups in the structure. Its solution in CH_2Cl_2 showed a strong i.r. absorption at 2 165 cm^{-1}, however, indicating that co-ordinated azido-groups are present, and isolation of the compound was not attempted. The i.r. spectrum was not identical over the whole range with that from decomposition of PN_9, as expected. The presence of azide in the product implies that equilibrium (1) occurs to some

$$2PCl_2(N_3) \rightleftharpoons PCl_3 + PCl(N_3)_2 \qquad (1)$$

extent. The concentration of $PCl(N_3)_2$ presumably remained below the detection limit in the ^{31}P n.m.r. spectrum; the rate of decomposition in mixtures of phosphorus(III) chloroazides was always in the order $P(N_3)_3 > PCl(N_3)_2 > PCl_2(N_3)$, so that removal of even a small amount of $PCl(N_3)_2$ by decomposition would disturb the equilibrium, causing more $PCl_2(N_3)$ to disproportionate. The alternative possibility of direct substitution by N_3^- into the chlorophosphazene polymer can be discounted, since a large excess of PCl_3 was used in this experiment in order to form the first substituted derivative only. The most telling point in favour of our interpretation of the nature of the decomposition products is that the compounds formed from $P(N_3)_3$ and $PCl_2(N_3)$ give identical ^{31}P n.m.r. spectra, but differing solution i.r. spectra, as expected.

The decomposition of $PBr_2(N_3)$ was investigated by adding a small amount of $Li[N_3]$ to excess of PBr_3 in CH_2Cl_2, and monitoring the ^{31}P n.m.r. spectrum at intervals. Decomposition occurred very slowly with liberation of N_2 to give three new resonances at 38.7, 71, and 80 p.p.m. Reaction between excess of PBr_3 and $Na[N_3]$ at high temperature is reported to give $(NPBr_2)_n$ polymers,[10] so similar products are expected here. The signal at 71 p.p.m. is readily assignable to $(NPBr_2)_4$,[1] but the remaining two signals cannot be assigned to simple known bromophosphazenes. Nevertheless, from the magnitudes of their chemical shifts they may reasonably be ascribed to $-PBr(N_3)=N-$ (38.7 p.p.m.) and $-PBr_2=N-$ (80 p.p.m.) units in a polymer chain. The signal at 80 p.p.m. was always the most intense (apart from that due to excess of PBr_3), suggesting that the postulated equilibrium between $PX_2(N_3)$ and more highly substituted species plays only a minor role here.

Attempts to prepare phosphorus(III) iodoazides were only partially successful. Thus PI_3 reacted vigorously with $Na[N_3]$ in MeCN solution to give $P(N_3)_3$, with rapid evolution of nitrogen gas. In addition to peaks of decomposition products at 4.9 and 12.9 p.p.m., a new high-field resonance at 178.9 p.p.m. was observed. The assignment of these signals is discussed below, but no peaks due to mixed phosphorus(III) compounds were found. In nitrobenzene, $Li[N_3]$ reacted with PI_3 to yield a new resonance at −162.0 p.p.m., assigned as $PI_2(N_3)$. No further substitution appeared to take place, and a complex pattern of decomposition products was found, with signals at 2.2, 12.9, 31.8, 55.8, 64.1, and 83.3 p.p.m. Evolution of N_2 continued even after no more phosphorus(III) species remained in solution. After 3 d, the spectrum had simplified somewhat, showing just three peaks at 2.2, 12.9, and 83.3 p.p.m.

Reaction of PI_3 with $Li[N_3]$ in the less polar solvent 1-iodopropane was much slower; a new signal at −162.2 p.p.m. [$PI_2(N_3)$] was present after a few hours, and a peak of a decomposition product at 87.1 p.p.m. was found after 1 d. On addition of more $Li[N_3]$ the resonance ascribed to $PI_2(N_3)$ increased greatly in intensity relative to that of PI_3, but no signals assignable to further substitution products could be detected. The solution evolved N_2 slowly, and the ^{31}P spectrum eventually showed just the two major decomposition products, at 14.5 and 85.1 p.p.m. No end-group resonance was apparent in the range 0—7 p.p.m., suggesting that the signal at 14.5 p.p.m. arises either from a cyclic polymer or from a long-chain species where the concentration of end groups would be relatively low. In CS_2 the reaction of PI_3 with $Li[N_3]$ was extremely slow, producing small amounts of $PI_2(N_3)$ (−161.3 p.p.m.) after several days. The substitution reaction could not be driven further, even by addition of a large excess of lithium azide.

In view of the ability of $Li[N_3]$ to replace chloride ligands in PCl_3 by azide in CS_2 as solvent, and its apparent reluctance to displace iodide, a system containing PCl_3, PCl_2I, $PClI_2$, and PI_3[23] was prepared by mixing PCl_3 and PI_3 in CS_2 solution. This was treated with $Li[N_3]$ in the hope that chloride would be preferentially substituted by azide. Only the known $PCl_{3-n}(N_3)_n$ series was found in the phosphorus(III) area, however, apart from a new signal at −170.9 p.p.m., ascribed to $PClI(N_3)$. No resonances were seen which could be unambiguously assigned to $PI_{3-n}(N_3)_n$ species, perhaps not surprisingly in the light of the shifts for $PCl_2(N_3)$ (Table 1) and $PI_2(N_3)$ in this solvent. Nevertheless the decomposition products of this system were not only those expected for $PCl_{3-n}(N_3)_n$. In addition to a peak at 17.8 p.p.m., strong resonances were observed at 87.1 and 114.6 p.p.m., suggesting that some mixed phosphorus(V) derivatives containing iodine are produced.

Identification of the decomposition products is by no means certain, but from the magnitudes of the chemical shifts some structural assignments may be made. Derivatives giving resonances between 0 and 20 p.p.m. may be assumed to contain no iodine, and are ascribed to $[-N=P(N_3)_2-]_x$ units in polymeric phosphazenes. The resonances between 83.3 and 87.1 p.p.m., at 114.6 p.p.m. (from the mixed Cl–I system), and at 178.9 p.p.m. (from the PI_3–$Na[N_3]$ reaction in MeCN) are almost certainly due to iodo-groups, and are assigned to $-N=PI(N_3)-$, $-N=P\text{-}ClI-$, and $-N=PI_2-$ units respectively in similar compounds. The signal at 87.1 p.p.m. clearly arises from a group which does not contain chlorine, since it occurs in the spectrum of the decomposition products from the PI_3–$Li[N_3]$ reaction in 1-iodopropane. Phosphonitrilic iodides do not seem to have been reported in the literature, but the shift difference for replacement of chloride by iodide in a phosphorus(V) compound looks reasonable by comparison with the results for the series $[PCl_nI_{3-n}(OH)]^+$ [24] and $PCl_nI_{3-n}S$.[25]

One further attempt to produce the mixed phosphorus(III) iodoazides was made by adding LiI to a solution containing PCl_3, $PCl_2(N_3)$, $PCl(N_3)_2$, and $P(N_3)_3$. Rapid decomposition occurred, however, giving rise to peaks at 10.7 and 17.8 p.p.m., and no evidence of substitution was found. We therefore conclude that phosphorus(III) iodoazides can be formed, as shown by the formation of PN_9 from PI_3 in MeCN, but that the intermediates are readily substituted by further azide in a polar solvent such as MeCN, although kinetically slow to react in a less polar solvent like CS_2. The compound $PI(N_3)_2$ has not been positively identified in any solvent, presumably because it is subject to such rapid substitution and/or decomposition that its concentration remains below the detection limit.

(*b*) $[PCl_{4-n}(N_3)_n][SbCl_6]$ ($0 < n < 4$) *and Decomposition Products*.—The preparation of $[P(N_3)_4][SbCl_6]$ from PCl_3 and $SbCl_4(N_3)$ dimer has been described by Schmidt;[6] the tetra-azidophosphonium ion gives a ^{31}P chemical shift of −11.8 p.p.m.[7] Attempted substitution of $[PCl_4][SbCl_6]$ by sodium azide in MeCN led to evolution of N_2, even at 253 K, however, and no azido-derivatives of

$[PCl_4]^+$ were obtained.[6] The nature of the decomposition products of $[P(N_3)_4]^+$ has not been established, and no cations intermediate between $[PCl_4]^+$ and $[P(N_3)_4]^+$ have been reported. By means of solution n.m.r. spectroscopy, we have identified all the possible intermediates, and can also account satisfactorily for the decomposition products.

Treatment of $[PCl_4][SbCl_6]$ with $Na[N_3]$ or $Li[N_3]$ in MeCN solution led to rapid evolution of N_2, in agreement with the work of Schmidt.[6] Phosphorus-31 n.m.r. signals from decomposition products were seen at -21.1, -15.0, -11.4, 5.8, and 8.9 p.p.m. In $MeNO_2$ solution, addition of $Li[N_3]$ to $[PCl_4][SbCl_6]$ caused the appearance of new peaks upfield from $[PCl_4]^+$, which can be readily assigned to $[PCl_{4-n}(N_3)_n]^+$ species: for $n = 0$—4, $\delta(^{31}P) = -87.1, -66.9, -46.7, -27.5$, and -11.4 respectively. The only uncertainty lies in the assignment of the signal at -11.4 p.p.m. to $[P(N_3)_4]^+$, since one of the major decomposition products also gives a resonance at -11.4 p.p.m., as discussed below. Nevertheless this result is in good agreement with the literature value,[7] so the signal may well be a composite, with contributions from both sources.

The peaks at -21.1 and 5.8 p.p.m. from the reaction in MeCN agree well with previous results for $(NPCl_2)_3$ and $(NPCl_2)_4$ respectively,[1] suggesting that these species and their azido-substituted derivatives are probably present in the decomposition products. The fully azido-substituted trimer $[NP(N_3)_2]_3$ has been prepared[26] and its i.r. and u.v. spectra recorded,[21,22] but no ^{31}P n.m.r. data were given. This compound was prepared in MeCN solution as described previously,[22,26] and gave a single ^{31}P n.m.r. signal at -11.4 p.p.m. (Table 2), in excellent agreement with one of the decomposition product peaks.

TABLE 2

Values of $\delta(^{31}P)$/p.p.m. for $(NPCl_2)_n$, $(NPBr_2)_n$, and their azido-derivatives

Compound		Azido-derivative
$(NPCl_2)_3$	-21.1	-11.4
$(NPCl_2)_4$	5.8	8.9
$(NPCl_2)_5$ [a]	17.0	
$(NPCl_2)_6$ [a]	16.0	
$(NPCl_2)_7$ [a]	18.0	
$(NPCl_2)_8$ [a]	18.0	
$(NPBr_2)_3$	43.6	-11.4
$(NPBr_2)_4$	75.8	8.9
Higher cyclic bromo-polymer [b]	95.1	16.2

[a] Ref. 1. [b] See text.

The compound $(NPCl_2)_4$ was similarly treated with excess of $Na[N_3]$ in acetonitrile and gave a single resonance at 8.9 p.p.m. (Table 2), agreeing perfectly with the highest-field signal from decomposition of the cations. No peaks between those of starting material and final product were detected in either case, suggesting that geminal substitution takes place. This conclusion was strongly supported by the results of reaction of $(NPCl_2)_3$ and $Na[N_3]$ in a 1 : 2 mol ratio. Only two resonances were found, at -21.1 and -11.4 p.p.m., in a 2 : 1 intensity ratio. This pattern could arise from a 2 : 1 mixture of $(NPCl_2)_3$ and $[NP(N_3)_2]_3$, or from the presence of a single species $\overline{N=P(N_3)_2-N=PCl_2-N=P}Cl_2$, but formation of either would necessarily involve geminal substitution. No intermediate signal was detected even when a limited amount of azide was added to a large excess of the trimer. This pattern probably arises because the electronegative azide group activates the phosphorus atom to which it is attached, making it very susceptible to further substitution.

The resonance at -15 p.p.m. observed from decomposition of the $[PCl_{4-n}(N_3)_n]^+$ systems could be due to a $-PCl(N_3)=N-$ unit in a trimer molecule, since the shift is intermediate between the groups $-PCl_2=N-$ and $-P(N_3)_2=N-$ in trimeric cyclophosphazenes. This is not inconsistent with the suggested pattern of substitution, since the species in this case is formed by decomposition involving loss of N_2, rather than by substitution. The decomposition products of the cations are thus deduced to be chloro- and azido-derivatives of cyclic phosphazene trimers and tetramers.

Reaction of $Na[N_3]$ with $(NPBr_2)_x$ species gave very similar results. A mixture of solid bromophosphazenes was prepared (Experimental section), and shown by n.m.r. in benzene solution to contain $(NPBr_2)_3$, $(NPBr_2)_4$, and a species giving a resonance at 95.1 p.p.m., probably a higher cyclic polymer (Table 2). Separation was not attempted since the compounds could be readily identified in solution.[1] The results from treatment with excess of $Na[N_3]$ in MeCN are shown in Table 2. Two of the signals are readily ascribed to the azido-substituted trimer and tetramer, and the remaining one to the higher cyclic polymer, similarly substituted. The identity of the decomposition products from the cation is thus amply confirmed.

(*c*) $[N(n\text{-}C_5H_{11})_4][PCl_{6-n}(N_3)_n]$ $(0 < n < 6)$.—The hexa-azidophosphate ion has been prepared previously by reaction of sodium azide with PCl_5 in MeCN solution.[8,9] A chemical shift of 184.1 p.p.m. has been reported,[9] but none of the possible mixed species was found. These have all been identified in solution by stepwise addition of $Li[N_3]$ to $[N(n\text{-}C_5H_{11})_4][PCl_6]$. Isomeric forms are possible for the ions with two to four azido-groups present, and structural assignments have been made on the basis of pairwise interactions.[27-29] A preliminary account of this work has been submitted for publication.[30]

In acetonitrile, $Na[N_3]$ reacted slowly with hexachlorophosphate to give only decomposition products, mainly polymeric phosphazenes [$\delta(^{31}P)$ 16.2 p.p.m.]. Smaller peaks were found at -21.1 and -9.8 p.p.m., possibly due to $(NPCl_2)_3$ and $[NP(N_3)_2]_3$. When $Li[N_3]$ was used, however, several resonances downfield from $[PCl_6]^-$ were seen, as well as decomposition products. Nitrogen was evolved from the solutions, which turned green in the process. Addition of a large excess of $Li[N_3]$ caused some substitution but mainly decomposition. The best method for observation of the various stages of substitution proved to be careful addition of successive small quantities of $Li[N_3]$ to a solution of the hexachlorophosphate in CH_2Cl_2. The ^{31}P n.m.r. spectrum was recorded after each addition, and from the changes in relative intensities as the reaction proceeded the resonances could be assigned to particular ions $[PCl_{6-n}(N_3)_n]^-$. Decomposition also took place during this time, and *ca.* 50% of the phosphorus in solution was in the form of decomposition products by the time complete substitution to $[P(N_3)_6]^-$ was achieved. For the ions $[PCl_{6-n}(N_3)_n]^-$ in CH_2Cl_2 solution, $\delta(^{31}P) = 298.2$, 243.5, 206.4, 183.4, 171.2, 167.7, and 180.0 p.p.m. for $n = 0$—6 respectively. The reaction was also carried out in MeCN and $MeNO_2$; the chemical shifts are essentially the same in each solvent. Ions containing up to four azide groups were relatively unstable in solution, decomposing completely within 1 d. Surprisingly, however, the more highly substituted species proved to be comparatively stable, and solutions containing $[P(N_3)_6]^-$ showed no sign of further decomposition after several months. In view of its explosive nature,[8,9] no attempt was made to isolate the compound.

Since only six resonances downfield from $[PCl_6]^-$ were seen in the six-co-ordinate region, the last to appear of which is readily assigned to $[P(N_3)_6]^-$,[9] it may be reasonably assumed that only one isomer is formed preferentially for the bis-, tris-, and tetrakis-(azido)-derivatives where two isomers are possible in each case. Structures can be assigned to each of the ions on the basis of pairwise interactions,[27-29] provided that certain assumptions are made. In this treatment, the chemical shift is considered to arise from interactions between the ligands attached to the central atom, which act along the edges of the co-ordination polyhedron, so that only interactions between adjacent groups have to be taken into account. For an octahedral species there are thus 12 pairwise-interaction terms, of three possible types only for chloroazides, corresponding to Cl–Cl, Cl–N_3, and N_3–N_3 interactions. The Cl–Cl term is taken as 24.9 p.p.m. from $[PCl_6]^-$, for which a shift of 298.2 p.p.m. was found in this work, in good agreement with previous results.[31] The Cl–N_3 term is then readily calculated from the experimental shift for $[PCl_5(N_3)]^-$ as 11.2 p.p.m. For $[PCl_4(N_3)_2]^-$, where *cis* and *trans* isomers are possible, the chemical shift of the *trans* form can be evaluated from the above data as 189.2 p.p.m., since there are no N_3–N_3 interactions. This is 17 p.p.m. lower than the experimental value, which is therefore assumed to arise from the *cis* isomer; hence the N_3–N_3 interaction term is calculated as 14.7 p.p.m. The chemical shift for all subsequent substituted derivatives, including the *mer* and *fac* isomers of $[PCl_3(N_3)_3]^-$ and the *cis* and *trans* (Cl) isomers of $[PCl_2(N_3)_4]^-$, can now be evaluated. The numbers thus obtained are compared with the experimental results in Table 3. Although perfect agreement is not obtained, it may reasonably be concluded that the trisubstituted derivative exists in the form of the *fac* isomer and the tetrasubstituted as the *cis* (Cl) isomer showing an overall pattern of *cis* substitution by azide groups. Support for the use of the pairwise-interaction method is provided by the experimental observation of the predicted upfield shift on going from $[PCl(N_3)_5]^-$ to $[P(N_3)_6]^-$.

Alternatively, if the assignment of the signal at 180.0 p.p.m. to $[P(N_3)_6]^-$ is assumed to be correct, the N_3–N_3 term works out as 15.0 p.p.m. The calculated shifts for $[PCl_3(N_3)_3]^-$, $[PCl_2(N_3)_4]^-$, and $[PCl(N_3)_5]^-$ are all slightly higher as a result, without changing the conclusions as to which isomers are present (Table 3). The predicted shift for *trans*-$[PCl_4(N_3)_2]^-$ does not vary since there is no N_3–N_3 term involved, and that calculated for *cis*-$[PCl_4(N_3)_2]^-$ is 206.7 p.p.m., in excellent agreement with the experimental result. The upturn in the shift values from $[PCl(N_3)_5]^-$ to $[P(N_3)_6]^-$ is predicted in this treatment also.

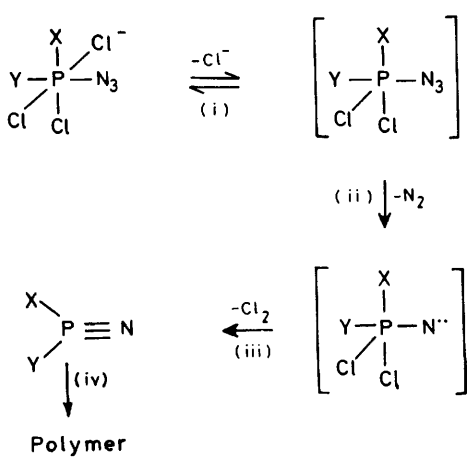
TABLE 3

Values of $\delta(^{31}P)$/p.p.m. predicted from pairwise-interaction terms for $[PCl_{6-n}(N_3)_n]^-$ ions

Ion	Calculated A	Calculated B	Experimental
$[PCl_4(N_3)_2]^-$ (*cis*)		206.7	206.4
(*trans*)	189.2	189.2	
$[PCl_3(N_3)_3]^-$ (*fac*)	186.0	186.9	183.4
(*mer*)	168.8	169.4	
$[PCl_2(N_3)_4]^-$ (*cis*)	165.6	167.1	171.2
(*trans*)	148.4	149.6	
$[PCl(N_3)_5]^-$	162.4	164.8	167.7
$[P(N_3)_6]^-$	176.4		180.0

A is calculated from N_3–N_3 term assuming disubstituted derivative is the *cis* isomer; B calculated using N_3–N_3 term from $[P(N_3)_6]^-$; Cl–Cl term from $[PCl_6]^-$, and Cl–N_3 term from $[PCl_5(N_3)]^-$.

A solution containing the less highly substituted azidochlorophosphates was allowed to decompose until no peaks were present in the six-co-ordinate region of the spectrum. A few drops of PCl_3 were then added to the green solution, which was immediately decolourised. The ^{31}P n.m.r. spectrum of the resultant liquid clearly showed the presence of $[PCl_6]^-$ and $[PCl_5(N_3)]^-$, suggesting strongly that Cl_2, $[N(C_5H_{11})_4]Cl$, and possibly ClN_3, are produced in the decomposition. The reactions for reformation of the six-co-ordinate ions would then be (2) and (3). Formation of $[PCl_5(N_3)]^-$ by substitution



SCHEME X,Y = Cl or N_3

into $[PCl_6]^-$ cannot be entirely discounted, although excess of azide was not expected to be present at this stage. A feasible mechanism for decomposition of the anions is shown in the Scheme. For the higher substituted derivatives, loss of chlorine in step (iii) could be

$$PCl_3 + Cl_2 + Cl^- \longrightarrow [PCl_6]^- \qquad (2)$$

$$PCl_3 + ClN_3 + Cl^- \longrightarrow [PCl_5(N_3)]^- \qquad (3)$$

replaced by loss of ClN_3. This mechanism could also account for the stability of $[PCl(N_3)_5]^-$ and $[P(N_3)_6]^-$; the initial step involving loss of Cl^- {or N_3^- for $[P(N_3)_6]^-$} would lead to a molecular species which is expected to be particularly unstable, so that there could be a kinetic barrier to its formation. Increasing substitution by azido-groups is expected, of course, to lead to a decrease in thermodynamic stability.

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