Organosubstituted Phosphazenes. Part 9.[1] Mass Spectra of Phenyl-substituted Chlorocyclophosphazenes

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Mass-spectral data for a series of phenylcyclotri-λ^5-phosphazenes, $N_3P_3Ph_nCl_{6-n}$ (n = 2—4 or 6), and isomeric tetrachlorotetraphenylcyclotetra-λ^5-phosphazenes, $N_4P_4Ph_4Cl_4$, of known structure are reported and discussed. Particular attention has been directed to developing correlations between fragmentation pattern and structure. Differentiation of molecules with diphenyl-substituted phosphorus atoms and molecules with mixed phenyl- and chloro-substituted phosphorus atoms is most clearly demonstrated in the tendency of the former derivatives to exhibit loss of hydrogen atoms and for the latter to undergo ready loss of chlorine atoms. Rearrangements, especially in the tetrameric series, make structural assignments based on low-mass fragments unreliable. With the aid of these correlations, the structure of a trace product from the reaction of MgBrPh and $N_4P_4Cl_8$ has been assigned from the mass-spectral data.

THERE has been recent interest in the application of mass spectrometry for the characterization of phosphazene derivatives. Initial work centered on detailed studies of the fragmentation patterns of the halogeno-[2-4] and pseudohalogeno-cyclophosphazene derivatives.[5] It has now become commonplace to find the major peaks of the mass spectra reported in the characterization data for new compounds.

Although there have been occasional applications of mass spectrometry to structure assignment, *e.g.* identification of anomalous products in the reactions of organomagnesium compounds with chlorocyclophosphazenes,[6,7] there has been little systematic attention given to the use of mass spectrometry as a structural tool. The mass spectra of a series of aryl-substituted fluorocyclotriphosphazenes have been examined and it was demonstrated that the different positional isomers exhibited different fragmentation processes.[8]

Since the occurrence of certain of the fragmentation patterns observed in this series appears to be related to the large difference in bond energy of the two substituents (fluorine and aryl moieties), it is of interest to examine a related series of compounds in which the bond-energy difference between the two substituents is reduced. In order to achieve this aim and to explore further the use of mass spectrometry as a structural tool, we have examined the mass spectra of a series of trimeric and tetrameric phenyl-substituted chlorocyclophosphazenes.

EXPERIMENTAL

Materials.—The following cyclophosphazenes were prepared by established procedures: $N_3P_3Ph_2Cl_4$, $N_3P_3Ph_4Cl_2$, and $N_3P_3Ph_6$,[9] and 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetra-λ^5-phosphazene.[10] A sample of *cis*-2,4,6-trichloro-2,4,6-triphenylcyclotri-λ^5-phosphazene was kindly provided by Professor R. A. Shaw. 4,4,8,8-Tetrachloro-2,2,6,6-tetraphenylcyclotetra-λ^5-phosphazene [6,11] was obtained from the Grignard synthesis described below.

Syntheses.—The reaction of octachlorocyclotetra-λ^5-phosphazene and phenylmagnesium bromide in toluene was allowed to proceed for 8 h at 110 °C in accordance with the procedure of Bode and Thamer.[12] The bulk of the reaction product was an intractible phosphazene polymer containing both phosphorus–chlorine and –phenyl groups. In addition to biphenyl and some unchanged $N_4P_4Cl_8$, the previously identified [6] compounds 4,4,6,6-tetrachloro-2-phenyl-2-triphenylphosphineiminocyclotri-λ^5-phosphazene, m.p. 176 °C, and 4,4,8,8-tetrachloro-2,2,6,6-tetraphenylcyclotetra-λ^5-phosphazene, m.p. 205 °C, were isolated.[5] A trace amount of a previously unreported diphenyl derivative $N_4P_4Ph_2Cl_6$, m.p. 115 °C, was also isolated. Mixtures of reaction products were separated by standard thin-layer chromatographic techniques using Merck silica gel G adsorbent with 13% calcium sulphate binder and carbon tetrachloride

[1] Part 8, C. W. Allen, *J. Organometallic Chem.*, 1977, **125**, 215.
[2] C. D. Schmulbach, A. G. Cook, and V. R. Miller, *Inorg. Chem.*, 1968, **7**, 2463.
[3] C. E. Brion and N. L. Paddock, *J. Chem. Soc.* (*A*), 1968, 388.
[4] C. E. Brion and N. L. Paddock, *J. Chem. Soc.*, (*A*), 1968, 392; G. E. Coxon, T. F. Palmer, and D. B. Sowerby, *ibid.*, 1967, 1958; 1968, 358.
[5] A. J. Wagner and T. Moeller, *J. Chem. Soc.* (*A*), 1971, 596.
[6] M. Biddlestone and R. A. Shaw, *J. Chem. Soc.*, (*A*), 1970, 1750.
[7] M. Biddlestone and R. A. Shaw, *J. Chem. Soc.* (*A*), 1971, 2715.
[8] C. W. Allen and P. L. Toch, *J.C.S. Dalton*, 1974, 1685.
[9] E. T. McBee, K. Okuhara, and C. J. Morton, *Inorg. Chem.*, 1965, **4**, 1672.
[10] R. A. Shaw and C. Stratton, *J. Chem. Soc.*, 1962, 5004.
[11] G. J. Bullen and P. E. Dann, *Acta Cryst.*, 1974, **B30**, 2861.
[12] H. Bode and R. Thamer, *Ber.*, 1943, **B76**, 521.

as the eluant. An ethanol–water solution of Methyl Red was used as the developer.*

Measurements.—The mass spectra of the trimeric derivatives were obtained on a single-focusing Atlas CH4-B mass spectrometer operating at 70 eV.† The spectra of the tetrameric derivatives were obtained on a CEC model 21-104 single-focusing mass spectrometer operating at 70 eV. Samples were admitted through the direct-inlet system.

RESULTS AND DISCUSSION

The mass-spectral data for the chlorophenylcyclotriphosphazenes, $N_3P_3Ph_nCl_{6-n}$ (n = 2—4 or 6), are in contrast, the mass spectrum of the non-geminal triphenyl derivative *cis*-2,4,6-$N_3P_3Ph_3Cl_3$ (4) does not exhibit peaks due to hydrogen abstraction from the parent ion, which is also consistent with the proposed mechanism. There is a trace (relative abundance = 0.3) of the peak at *m/e* 183 in the spectrum of (4), but it presumably arises from a rearrangement process. Curiously, the hexaphenyl derivative $N_3P_3Ph_6$ (3) does not undergo hydrogen abstraction, but forms protonated ions.

It has been observed that the solution basicity (in nitrobenzene towards perchloric acid) of (3) is considerably greater than (1), (2), or (4).[17] Hence, it may be that the gas-phase basicity of (3) is sufficient to allow for ready protonation. Protonated fragments have been detected in the mass spectra of other phosphazene

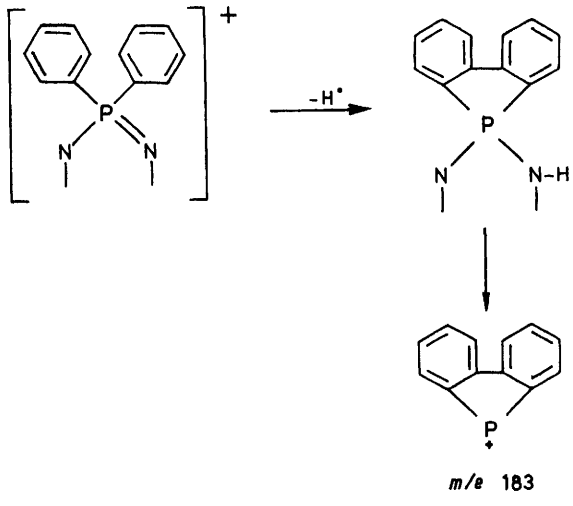
TABLE 1

Selected mass spectra for phenyl-substituted chlorocyclotriphosphazenes [a]

2,2-$N_3P_3Ph_2Cl_4$ (1) [b,c]			2,2,4,4-$N_3P_3Ph_4Cl_2$ (2) [b,d]			$N_3P_3Ph_6$ (3) [e]			*cis*-2,4,6-$N_3P_3Ph_3Cl_3$ (4) [f]		
m/e	Relative abundance	Assignment	*m/e*	Relative abundance	Assignment	*m/e*	Relative abundance	Assignment	*m/e*	Relative abundance	Assignment
429	39.1	$[N_3P_3Ph_3Cl_4]^+$	513	10.0	$[N_3P_3PhCl_3]^+$	599	6.0	$[N_3P_3H_2Ph_4]^+$	471	17.0	$[N_3P_3Ph_2Cl_3]^+$
428	100.0	$[N_3P_3Ph(C_6H_4)Cl_4]^+$	512	64.7	$[N_3P_3Ph_3(C_6H_4)Cl_2]^+$	598	40.7	$[N_3P_3HPh_4]^+$	436	100.0	$[N_3P_3Ph_3Cl_2]^+$
394	20.9	$[N_3P_3Ph_2Cl_3]^+$	511	100	$[N_3P_3Ph_2(C_6H_4)_2Cl_2]^+$	597	100.0	$[N_3P_3Ph_5]^+$	401	0.7	$[N_3P_3Ph_2Cl]^+$
392	9.9	$[N_3P_3(C_6H_4)_2Cl_3]^+$	478	13.8	$[N_3P_3Ph_4Cl]^+$	522	2.3	$[N_3P_3H_2Ph_5]^+$	394	0.2	$[N_3P_3Ph_2Cl_3]^+$
358	2.0	$[N_3P_3Ph(C_6H_4)Cl_2]^+$	477	12.1	$[N_3P_3Ph_3(C_6H_4)Cl]^+$	521	7.6	$[N_3P_3HPh_5]^+$	355	2.2	$[N_3P_2Ph_2(C_6H_4)Cl]^+$
352	28.1	$[N_3P_3PhCl_4]^+$	476	5.2	$[N_3P_3Ph_2(C_6H_4)_2Cl]^+$	520	85.3	$[N_3P_3Ph_5]^+$	324	2.3	$[N_3P_3Ph_2Cl]^+$
324	2.1	$[N_3P_3Ph_2Cl]^+$ (?)	436	23.4	$[N_3P_3Ph_3Cl_2]^+$	444	10.9	$[N_3P_3HPh_4]^+$	235.5	1.1	$[N_3P_3Ph_3Cl_3]^{2+}$
313	7.2	$[P-Cl_2PNH]^+$ (?)	400	1.7	$[N_3P_3Ph_2(C_6H_4)Cl]^+$	442	3.3		234	1.1	
312	2.8		359	3.6	$[N_3P_3Ph_2Cl_2]^+$	397	2.9		217.5	1.9	$[N_3P_3Ph_3Cl_2]^{2+}$
282	9.9	$[N_3P_3PhCl_3]^+$	324	2.7	$[N_3P_3Ph_2Cl]^+$	366	4.1	$[N_3P_3Ph_3]^+$	200.5	1.5	$[N_3P_3Ph_3Cl]^{2+}$
276	5.8	$[N_3P_3Cl_4H]^+$	282	2.9	$[N_3P_3PhCl_2]^+$	321	2.9		198	2.4	*g*
271	4.9		256.5	1.1	$[N_3P_3Ph_4Cl_2]^{2+}$	306	1.9		143	2.4	$[PPhCl]^+$
261	1.3	$[N_3P_3Cl_4]^+$	239	1.0	$[N_3P_3Ph_4Cl]^{2+}$	298.5	30.2	$[N_3P_3Ph_6]^{2+}$	122	4.0	$[PNPh]^+$
214.5	5.4	$[N_3P_3PhCl_4]^{2+}$	198	3.5	*g*	290	0.8	$[N_3P_3HPh_5]^+$	77	2.7	$[C_6H_5]^+$
214	1.9	$[N_3P_3Ph(C_6H_4)Cl_4]^{2+}$	183	2.5	$[PC_{12}H_8]^+$	277	3.5				
198	16.2	*g*	122	4.4	$[PNPh]^+$	275	1.35	$[N_3P_3Ph_2]^+$			
183	7.3	$[PC_{12}H_8]^+$	77	4.5	$[C_6H_5]^+$	260	47.3	$[N_3P_3Ph_5]^{2+}$			
122	15.2	$[PNPh]^+$				198	12.0	*g*			
						185	3.9	$[PPh_2]^+$			
77	13.9	$[C_6H_5]^+$				183	11.2	$[PC_{12}H_8]^+$			
						122	9.7	$[PNPh]^+$			
						77	1.9	$[C_6H_5]^+$			

[a] Monoisotopic based on ^{35}Cl. When peaks are separated by a small number of mass units, the intensities have been corrected for chlorine and carbon isotope distribution where appropriate. Peaks below *m/e* 77 and/or relative abundance <1 are not reported [b] The *m/e* <300 region contains several low-intensity peaks which are difficult to differentiate from the background and so are unreported. [c] Probe at 40, source at 216 °C. [d] Probe at 40, source at 220 °C. [e] Probe at 180, source at 230 °C. [f] Probe at 110, source at 190 °C. [g] $[P(C_6H_4)_2NH]^+$ or $[N_2P_3Ph]^+$: equally reasonable assignments.

Table 1. The geminal diphenyl and tetraphenyl derivatives, 2,2-$N_3P_3Ph_2Cl_4$ (1) and 2,2,4,4-$N_3P_3Ph_4Cl_2$ (2), show complex peaks in the parent-ion region due to the loss of one hydrogen atom per PPh_2 unit. The ions due to loss of hydrogen atoms represent the 100% peak in each case. Intense peaks of this type are very common in phenyl–phosphorus compounds containing more than one phenyl group attached to the phosphorus atom.[13–16] This process is believed to lead to the stable phosphafluorenyl ion and eventually to $[PC_{12}H_8]^+$ (*m/e* 183) as shown below.[13] This proposal is consistent with the observation of loss of one hydrogen atom from (1) and two hydrogen atoms from (2). Furthermore, in each case there is a peak at *m/e* 183 but not at 185. In



* This developer is superior to others used and is prepared by diluting a saturated solution of Methyl Red in water (25 °C) with an equal volume of ethanol. The pH of the developer is adjusted to 7.0 with dilute sodium hydroxide. The indicator gives red spots for the chloro- and chlorophenyl-cyclophosphazenes and biphenyl. Hydrolysis products of the phosphazenes, phenylphosphonic acid, diphenylphosphinic acid, and orthophosphoric acid also give red spots, while triphenylphosphine oxide is indicated by an orange spot.

† Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

[13] J. C. Tebby, in 'Organophosphorus Chemistry,' vol. 1, ed. S. Tippett, The Chemical Society, London, 1970, p. 318.
[14] D. H. Williams, R. S. Ward, and R. G. Crooks, *J. Amer. Chem. Soc.*, 1960, **90**, 966.
[15] L. Tokes and S. C. K. Wong, *Org. Mass Spectrometry*, 1970, **4**, 59.
[16] T. R. Spalding, *Org. Mass Spectrometry*, 1976, **11**, 1019.
[17] D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *J. Chem. Soc.*, 1965, 2804; D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1969, 196.

derivatives.[8,18] Ring-nitrogen protonation would serve to block formation of the phosphafluorenyl ion. The peak at *m/e* 183 in the spectrum of (3) may arise from the $\equiv[PPh_2]^+$ (*m/e* 185) ion (which is observed in this case) by loss of two hydrogen atoms (sequentially or as H_2). It is interesting to note that geminal dialkyl tetraphenylcyclotriphosphazenes are reported to exhibit significant amounts of hydrogen abstraction from the parent ions.[19] However, it has not been established whether the hydrogen abstraction is from the alkyl or aryl group.

In the mass spectra of (1) and (2) one observes that the loss of a phenyl group or a chlorine atom from the parent ion occur with similar probability (as judged by the relative abundance of the resulting ions). This observation is in contrast to the corresponding fluoro-derivatives where the strong P–F bond preferentially remains intact.[8] Furthermore, the linear ions, *e.g.* $[N_2P_3X_n]^+$ and $[NP_2X_n]^+$, which are important in the fluoro-derivatives are not found in any significant abundance in the spectra of (1) and (2). The remainder of the fragmentation pattern of (3) is dominated by the loss of the first phenyl group and by large amounts of doubly charged ions.

The fragmentation behaviour of (4) is quite different from that of (1) and (2). In this case, the 100% peak corresponds to the $[P - 35]^+$ ion.* This species presumably arises from elimination of a chlorine atom from the parent ion. The loss of a phenyl group from the parent ion is minimal in the mass spectrum of (4). The strong preference for formation of the $[P - 35]^+$ ion in this case can be correlated with the available structural data for the chlorophenylcyclophosphazenes which show longer P–Cl bond lengths in PPhCl than in PCl_2 environments.[11,18,20] Correlations of ^{35}Cl n.q.r. frequencies with P–Cl bond lengths in cyclophosphazenes have also been established.[21] Since there is considerable polarization of the phenyl electron density towards the phosphorus atom in phenyl-substituted cyclophosphazenes,[1] one would expect an even more significant polarization in a $\overset{+}{P}Ph$ centre and hence the possibility of greater stabilization of the ion derived from the loss of chlorine from a PPhCl than a PCl_2 centre. The lability of the P–Cl bond in a PPhCl environment is also suggested by the isolation of only derivatives containing PPh_2 in the Friedel–Crafts reaction of $N_3P_3Cl_6$.[9]

One should also consider the additional possibility of stabilization of the P–Cl bond in the geminally substituted derivatives when accounting for the difference in abundance of the $[P - 35]^+$ peak relative to the parent ion. Although the effect is not as large as in the mass spectrum of (4), the $[P]^+ : [P - 35]^+$ ratio in $N_3P_3Cl_6$ and $N_4P_4Cl_8$ is less than 1 : 1.[2] Consequently, that the observed $[P - 1]^+ : [P - 35]^+$ ratio is > 1 : 1 in (1) and (2) may indicate that the P–Cl bond is strengthened in the geminal derivatives.

Although the available structural data do not provide any justification for this claim, it has been observed that the rate of substitution at the P–Cl bond decreases in the order $N_3P_3Cl_6 > (1) > (2)$.[22] Kinetic evidence should be used with caution since we are assuming that thermodynamic effects are predominant in determining the relative abundance of ions in the mass spectrum. Furthermore, if kinetic effects are important in determining the ion abundance in the mass spectra, then the rates of decomposition to ions of lower mass may also be significant. The remainder of the spectrum of (4) consists of low-intensity peaks due mostly to P–Ph and P–Cl bond cleavage.

The mass-spectral data for three isomeric tetrachlorotetraphenylcyclotetraphosphazenes are in Table 2. As might be expected, the fragmentation is more complex than that of the trimeric derivatives. In general, the spectra of all the isomers exhibit high abundances of low-mass fragments and in each case the base peak of the spectrum is $[C_6H_5]^+$. All the isomers show fragments derived from ring contraction, *i.e.* formation of N_3P_3 derivatives, and the formation of linear units, *e.g.* N_2P_3 and NP_2 species. Similar behaviour has been observed in the mass spectrum of $N_4P_4Cl_8$.[2,3]

There is evidence of rearrangement processes, *e.g.* the peak at *m/e* 91 has been assigned to the $[NPh]^+$ ion on the basis of deuterium labelling in the spectra of fluorophenylcyclotriphosphazenes.[8] It is reasonable to assume the same assignment in this series. Thus, phenyl-group migration occurs from phosphorus to nitrogen atoms. A significant peak at *m/e* 183 is observed in both the geminal, 2,2,6,6-$N_4P_4Ph_4Cl_4$ (7), and non-geminal tetraphenyl derivatives, α-*trans*-2,4,6,8-$N_4P_4Ph_4Cl_4$ (5) and β-*trans*-2,4,6,8-$N_4P_4Ph_4Cl_4$ (6). Assuming that the assignment of this peak to the $[PC_{12}H_8]^+$ ion is correct, a rearrangement process occurs giving rise to a diorganosubstituted phosphorus atom from non-geminal precursors (5) and (6). In a similar case, the observation of the peak at *m/e* 143, $[PPhCl]^+$, for the geminal derivative (7) indicates another significant rearrangement. Therefore, the observation of low-mass fragments of a particular composition cannot be used to establish the structure of the parent phosphazene.

The existence of the $[P - 1]^+$ fragments allowed differentiation of geminal and non-geminal phenyl-substituted cyclotriphosphazenes. Unfortunately, the resolution of the instrument used to collect the data for the tetrameric derivatives was insufficient to distinguish unambiguously between the isotopic distribution peaks due to the parent ion and those of the $[P - 1]^+$ ion. Fortunately, the other major structure-defining probe, the ratio of the abundance of the parent to that of the $[P - Cl]^+$ ion, is still easily correlated with the positional

* $[P - 35]^+$ represents the ion which is 35 mass units below the mass of the parent (P) ion.

[18] T. Chivers and R. Hedgeland, *Canad. J. Chem.*, 1972, **50**, 1017.
[19] R. Appel and G. Saleh, *Chem. Ber.*, 1973, **106**, 3455.
[20] G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 1651.
[21] R. Keat, A. L. Porte, D. A. Tong, and R. A. Shaw, *J.C.S. Dalton*, 1972, 1648.
[22] K. Hills and R. A. Shaw, *J. Chem. Soc.*, 1964, 130.

isomerism in the system in question. Thus, the spectra of the non-geminal isomers (5) and (6) exhibit $[P]^+$: $[P - Cl]^+$ ratios which are significantly less than 1 : 1, whereas the $[P]^+$: $[P - Cl]^+$ ratio for the geminal isomer (7) is > 1 : 1. As in the trimeric series, this observation can be related to the fact that the P–Cl bond length in (6) [and presumably (5)] is longer than in a geminal PCl_2 arrangement.[11] The generality of the preferential loss of a labilized chlorine atom in this series of compounds suggests that mass spectrometry may be a useful probe for distinguishing geminal and non-geminal isomers in other chlorophosphazenes with labilized chlorine atoms, *e.g.* amino-derivatives.

It is also worth noting that the $[P - 77]^+$ ion, *i.e.* $[P - Ph]^+$, is observed in the spectrum of (7), but not in the spectra of the non-geminal isomers (5) and (6). The $[P - 77]^+$ and $[P - 35]^+$ ions are observed in roughly similar abundances in the mass spectra of the geminal derivatives in the trimeric series [(1) and (2)]. However, the $[P - 77]^+$ ion is only detected at trace levels in the spectrum of the non-geminally substituted trimeric derivative (4). The reason for the decrease in the amount of the $[P - 77]^+$ ion relative to the $[P - 35]^+$ ion on going to the tetrameric derivative is unclear.

The reaction between MgBrPh and $N_4P_4Cl_8$ in toluene produces, in addition to the previously reported compounds,[6] a few trace products. One of these, (8), m.p. 115 °C, was isolated (chromatographically) and the i.r. and mass spectra were obtained. The mass-spectral data are in Table 3. The highest *m/e* value (assumed to be that of the parent ion) and the isotope pattern establish the molecular formula as $N_4P_4Ph_2Cl_6$. The i.r. spectrum [ν(NPN) at 1 315vs and 1 300vs] provides strong evidence for a tetrameric phosphazene containing phenyl groups.

The mass spectrum of (8) is similar to other phenylcyclotetraphosphazenes in that low-mass fragments are highly abundant with the $[C_6H_5]^+$ ion being the base peak. The spectrum exhibits a variety of linear fragments which are found in the spectrum of $N_4P_4Cl_8$.[2,3]

TABLE 2

Selected mass spectra of $N_4P_4Ph_4Cl_4$ isomers [a]

Assignment	*m/e*	Relative abundance: 2,4,6,8-$N_4P_4Ph_4Cl_4$ [b] (5)	2,4,6,8-$N_4P_4Ph_4Cl_4$ [c] (6)	2,2,6,6-$N_4P_4Ph_4Cl_4$ [d] (7)
$[N_4P_4Ph_4Cl_4]^+$	628	2.6	8.2	17.0
$[N_4P_4Ph_4Cl_3]^+$	593	10.6	24.6	9.7
$[N_4P_4Ph_4Cl_2]^+$	558	2.6	4.5	2.6
$[N_4P_4Ph_3Cl_4]^+$	551			3.4
$[N_3P_3(C_6H_4)_4Cl_2]^+$	513	0.8	1.2	1.5
$[N_3P_3Ph_4Cl]^+$	478	1.1	1.8	1.1
$[N_3P_3Ph_3Cl_2]^+$	436		3.3	
$[N_2P_3Ph_3Cl_2]^+$	422	3.8	0.1	11.0
$[N_3P_3Ph_2Cl_3]^+$	394	0.9	1.1	3.2
$[N_3P_4Ph_2Cl]^+$	355	2.5	3.2	2.4
$[N_3P_3Ph_2Cl]^+$	324	2.8	3.6	1.7
$[N_4P_4Ph_4Cl_4]^{2+}$	314	5.0	7.4	10.2
$[NP_2Ph_2Cl_2]^+$	300	1.3	1.9	3.7
$[N_4P_4Ph_4Cl_3]^{2+}$	296.5	5.0	6.1	7.2
$[N_4P_4Ph_4Cl_2]^{2+}$	279	10.2	13.3	8.7
$[NP_2Ph_2Cl]^+$	265	4.4	5.3	9.5
?	261	8.7	11.5	5.3
$[N_2P_3PhCl]^+$	233	3.7	4.8	2.6
$[NP_2PhCl_2]^+$	223	2.4	2.8	2.4
$[N_3P_3Ph]^+$ (?)	212	2.8	3.5	4.1
e	198	15.8	19.2	24.4
$[PC_{12}H_8]^+$	183	5.6	6.5	18.8
$[N_2P_2Ph]^+$ (?)	167	7.9	8.8	7.9
$[PPhCl]^+$	143	29.1	36.1	31.4
$[PNPh]^+$	122	57.4	66.5	78.6
$[NP_2Cl]^+$	111	4.9	2.1	3.0
$[PC_6H_4]^+$	107	14.1	15.4	17.1
$[PCl_2]^+$	101		0.8	1.6
$[NPh]^+$	91	7.2 [f]	2.7	9.7
$[C_6H_5]^+$	77	100.0	100.0	100.0

[a] Monoisotopic peaks based on ^{35}Cl. Peaks below *m/e* 77 are not reported. Several low-intensity peaks which occur below *m/e* 260, and a series of moderate-intensity unassigned peaks which occur at *m/e* 154—160 are not reported. [b] M.p. 153 °C. Assigned to the α-*trans* isomer [10] (B. Grushkin, A. J. Berlin, J. M. McClanahan, and R. G. Rice, *Inorg. Chem.*, 1966, **5**, 172), *i.e.* one phenyl group *trans* to the other three. Probe at 70, source at 250 °C. [c] M.p. 248 °C. Assigned to the β-*trans* isomer (A. H. Burr, C. H. Carlisle, and G. J. Bullen, *J.C.S. Dalton*, 1974, 1659), *i.e.* two phenyl groups are *trans* to the other two phenyl groups. [d] M.p. 205 °C, isolated from the Grignard reaction. Assigned to the geminal isomer with phenyl group on alternate phosphorus atoms.[11] [e] $[P(C_6H_4)_2NH]^+$ or $[N_2P_3Ph]^+$ are equally reasonable assignments. [f] Large numbers of peaks of this intensity in the range *m/e* 80—100.

TABLE 3

Selected mass spectra of $N_4P_4Ph_2Cl_6$ (8) [a]

Assignment	*m/e*	Relative abundance
$[N_4P_4Ph_2Cl_6]^+$	544	3.1
$[N_4P_4Ph_2Cl_5]^+$	509	1.3
$[N_4P_4PhCl_6]^+$	467	0.6
$[N_4P_4PhCl_5]^+$	432	0.6
$[N_3P_3PhCl_5]^+$	387	0.1
$[N_3P_3PhCl_4]^+$	352	1.5
$[N_3P_3Cl_5]^+$	310	0.7
$[N_3P_3PhCl_2]^+$	282	0.5
$[N_4P_4Ph_2Cl_6]^{2+}$	272	0.3
?	261	0.8
$[N_4P_4Ph_2Cl_5]^{2+}$	254.5	0.8
$[N_3P_3Cl_3]^+$	240	1.3
?	237	1.5
$[NP_2Cl_4]^+$	216	1.0
b	198	4.7
$[PC_{12}H_8]^+$	183	2.1
$[N_2P_2Ph]^+$	167	1.4
[NPPhCl]	157	7.8
$[NP_2Cl_2]^+$	146	4.8
$[PPhCl]^+$	143	9.2
$[PNPh]^+$	122	29.1
$[NP_2Cl]^+$	111	3.3
$[PC_6H_4]^+$	107	11.7
$[PCl_2]^+$	101	37
$[NPh]^+$	91	2.9
$[C_6H_5]^+$	77	100

[a] Monoisotopic peaks based on ^{35}Cl. Most low-intensity unidentified peaks below *m/e* 280 are not reported; source at 110, probe at 248 °C. [b] $[P(C_6H_4)_2NH]^+$ or $[N_2P_3Ph]^+$ are equally reasonable assignments.

The only unusual feature is the anomalously low abundance of doubly charged ions. The $[P]^+$: $[P - Cl]^+$ ratio is significantly greater than 1 : 1 and both $[P - 77]^+$ and $[P - 35]^+$ ions are observed so a geminal configuration of phenyl groups is the most probable structural assignment. Since there is only one possible geminal isomer for a molecule with the $N_4P_4X_6Y_2$ formulation, compound (8) appears to be 4,4,6,6,8,8-hexachloro-2,2-

diphenyl-λ^5-tetraphosphazene. As in the case of the tetrachlorotetraphenylcyclotetraphosphazenes (5)—(7), ions are observed which are indicative of rearrangement processes. In particular, the ions at *m/e* 91 ($[NPh]^+$), 143 ($[PPhCl]^+$), and 387 ($[N_3P_3PhCl_5]^+$) clearly must arise by rearrangement processes similar to those observed for compounds (5)—(7).

In conclusion, a detailed examination of the mass spectra of phenyl-substituted chlorocyclo-triphosphazenes and -tetraphosphazenes has uncovered processes which can be related to the positional isomer under consideration. Application of these generalizations has allowed the structural assignment of a trace product from the reaction of MgBrPh with $N_4P_4Cl_8$. The danger of attempting to assign structure on the basis of low-mass fragments has been established by the observation of a variety of ions which arise through rearrangement processes.

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