Reactions of Alkali-metal Azides with some Organophosphorus(V) Compounds

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The reactions of $Li[N_3]$ or $Na[N_3]$ with some organophosphorus(V) compounds containing chloro-groups, including $PCl_5(py)$ (py = pyridine) and catechyl derivatives of PCl_5, have been investigated by ^{31}P n.m.r. spectroscopy. Several new azido-species have been identified in solution. In the $PCl_5(py)$ system, where isomerism is possible, configurations have been assigned by the method of pairwise interactions.

MUCH work has been carried out on the preparation and properties of four-co-ordinate organophosphorus(V) azides.[1-4] Compounds of the type $PR_2(N_3)X$, $P(N_3)(OR)_2X$, $P(N_3)(NHR)_2O$, and $PR(N_3)_2X$, where X = S or O and R = an organo-group, have been reviewed recently.[2] Schmidt and co-workers[3,4] have also synthesised, and obtained ^{31}P n.m.r. data for, the azido-cations in $[PMe_{4-n}(N_3)_n][SbCl_6]$ and $[PPh_{4-n}(N_3)_n][SbCl_6]$ ($1 \leqslant n \leqslant 3$). No reports have appeared, however, on five- or six-co-ordinate organophosphorus(V) azides. In a recent paper we described the reaction of alkali-metal (Li or Na) azides with some inorganic halogenophosphorus compounds.[5] These investigations have now been extended to organophosphorus compounds containing chloro-groups, including some five- and six-co-ordinate species such as $PCl_5(py)$ (py = pyridine) and catechyl derivatives of phosphorus(V) chloride.

EXPERIMENTAL

All manipulations, including preparation of samples for ^{31}P n.m.r. spectroscopy, were carried out under an inert atmosphere of dry nitrogen. The compounds $PCl_3(O_2C_6H_4)$ and $PCl(O_2C_6H_4)_2$ were prepared by reaction of *o*-dihydroxybenzene (catechol) and PCl_5 in the appropriate molar ratios,[6] while other organophosphorus compounds were prepared as described previously[7,8] or elsewhere,[9] and lithium azide by the method of Hoffman-Bang.[10] All other chemicals were of the best available commercial grade and used without further purification, except for tetra-n-pentylammonium chloride which was thoroughly dried before use.[5] Sample preparation and the destruction of residues containing azido-species were carried out as indicated in a previous paper.[5] Isolation of solid compounds was not attempted in view of the probable explosive nature of the products.[1-5]

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on a Fourier-transform spectrometer,[11] using stationary sample tubes (outside diameter 8.4 mm). Chemical shifts were measured relative to external 85% H_3PO_4, and are quoted with the downfield direction taken as positive.

RESULTS AND DISCUSSION

Azido-derivatives of PCl_5 *and* $PCl_5(py)$.—When a small amount of $Li[N_3]$ or $Na[N_3]$ was added to a solution of PCl_5 in $PhNO_2$ the ^{31}P n.m.r. spectrum of the solution, after reaction had subsided, showed the presence of $(NPCl_2)_3$ (δ 21.1 p.p.m.)[12] together with some unreacted PCl_5. Addition of larger quantities of $Li[N_3]$ caused a violently exothermic reaction. The resultant ^{31}P n.m.r. spectrum contained major peaks at 8.2 and −12.2 p.p.m., possibly with fine structure due to coupling between inequivalent phosphorus nuclei, which almost certainly arise from polymeric phosphazenes.[5] The results suggest that molecular azido-derivatives of PCl_5 are particularly unstable.

Since PCl_6^- reacted with $Li[N_3]$ to give substitution products,[5,13] an attempt was made to obtain more stable molecular species from the six-co-ordinate compound $PCl_5(py)$.[7] Initially CH_2Cl_2 was used as solvent; reaction of $Li[N_3]$ with $PCl_5(py)$ was accompanied by gentle effervescence. The n.m.r. spectrum showed a small resonance at −197.5 p.p.m., assigned to $PCl_4(N_3)(py)$, although the main reaction products were again phosphazene derivatives, with resonances at 3.3, −5.8 $[(NPCl_2)_4]$,[12] −8.9 $\{[NP(N_3)_2]_4\}$,[5] and −12.9 p.p.m. The reaction was repeated in pyridine as solvent to suppress any dissociation of the complex. Careful addition of successive small quantities of $Li[N_3]$ caused no evolution of N_2, and the new resonances observed in the ^{31}P n.m.r. spectra could be assigned to particular species from the variation in intensity with amount of azide, as shown in Table 1. The final product gave a resonance at −178.9 p.p.m., in good agreement with the shift for $P(N_3)_6^-$,[5,13,14] suggesting that at some stage in the reaction the co-ordinated pyridine is displaced by azide.

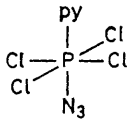
TABLE 1

$\delta(^{31}P)$ (p.p.m.) for $PCl_{5-n}(N_3)_n(py)$ in pyridine

n	0	1	2	3	4
δ	−231.3	−199.6	−159.7	−165.5	−171.9

The possibility of isomerism arises in this series, and the method of pairwise interactions[13,15-17] for identification of the particular isomer present can be applied, if it is assumed that the pairwise parameters for an octahedral phosphorus(V) complex are independent of the charge, so that the Cl : Cl term can be taken from PCl_6^- and the $N_3 : N_3$ term from $P(N_3)_6^-$. This enables the py : Cl term to be evaluated as −8.2 p.p.m. from the shift of $PCl_5(py)$. The shift of the *trans* isomer (I) can now be calculated as −177.2 p.p.m., since there are no py : N_3 terms involved. This value is considerably different from that of −199.6 p.p.m. observed for $n = 1$ in Table 1, suggesting that the compound $PCl_4(N_3)(py)$

has a *cis* configuration. Hence the py : N_3 term is evaluated as −17.1 p.p.m., giving sufficient information to allow the chemical shifts of all subsequent isomers to be calculated, as shown in Table 2. The course of reaction thus appears to be that shown in Scheme 1. Step (iv) is not completely unambiguous since the observed shift for $PCl(N_3)_4(py)$ lies between the values calculated for the two possible isomers, but a change in configuration from the previous compound, the results for which clearly indicate an azido-group *trans* to py, is most unlikely.

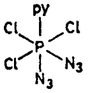
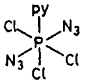
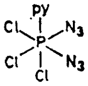
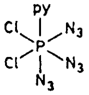
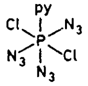
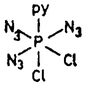
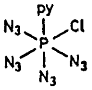
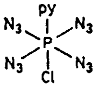


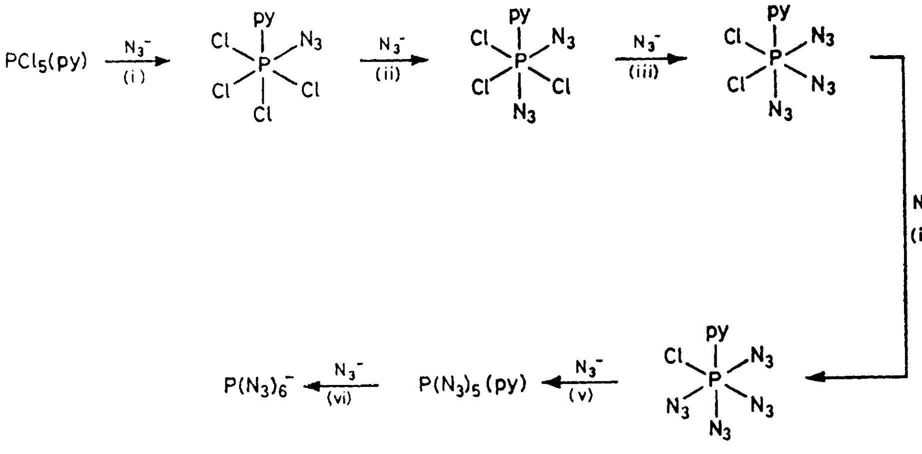
(I)

The shift of the resonance assigned to $PCl(N_3)_4(py)$ is similar to the value of −171.2 p.p.m. observed for $PCl_2(N_3)_4^-$ in CH_2Cl_2.[13] No signal attributable to $PCl(N_3)_5^-$ was observed, however, and since this ion is fairly stable kinetically [5] it should have been apparent in the n.m.r. spectrum if reaction proceeded *via* $PCl_2(N_3)_4^-$. We therefore conclude that the resonance at −171.9 p.p.m. is correctly assigned as $PCl(N_3)_4(py)$, and that this species reacts readily with azide ion to give the (unobserved) $P(N_3)_5(py)$, which itself reacts rapidly with N_3^- to displace the pyridine molecule, yielding $P(N_3)_6^-$. This deduction is supported by the consistently low intensity of the resonance at −171.9 p.p.m. Only comparatively small amounts of decomposition products were observed during the reaction, identified as $[NP(N_3)_2]_4$ (δ −8.2 p.p.m.) [5] and polymeric phosphonitrilic chloride and/or azide (δ −14.5 p.p.m.).[5]

TABLE 2

Calculated and observed shifts (p.p.m.) for $PCl_{5-n}(N_3)_n(py)$ ($2 \leqslant n \leqslant 5$)

Compound	Structure	$\delta_{calc.}$	$\delta_{obs.}$
$PCl_3(N_3)_2(py)$		−163.0	−159.7
		−168.0	
		−185.3	
$PCl_2(N_3)_3(py)$		−166.2	−165.5
		−148.6	
		−171.0	
$PCl(N_3)_4(py)$		−168.9	−171.9
		−174.0	
$P(N_3)_5(py)$	One isomer	−189.2	

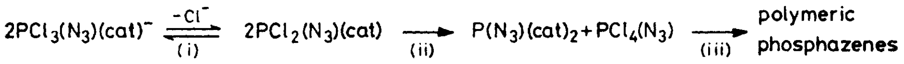


SCHEME 1

Azido-derivatives of Catechylphosphorus(V) *Chlorides*.—Addition of $Li[N_3]$ to a solution of $PCl(O_2C_6H_4)_2$ [= $PCl(cat)_2$] in CH_2Cl_2 gives rise to a single new resonance at −26.7 p.p.m., assigned to $P(N_3)(cat)_2$, without evolution of N_2. The product is probably stable in solution because there is no facile route of decomposition to a polymeric phosphazene, unlike azides derived from PCl_5. When $[N(n\text{-}C_5H_{11})_4]Cl$ was added to the solution, a new resonance appeared at −112.9 p.p.m. This signal increased in intensity with the addition of more Cl^-, and is assigned to $PCl(N_3)(cat)_2^-$. No decomposition was apparent, the only other peak seen being that (−30.7 p.p.m.) [18] due to $P(cat)_2(OH)$, formed by partial hydrolysis of $P(cat)_2Cl$. This resonance also moved upfield to −83.1 p.p.m. on addition of Cl^-, presumably due to the formation of $PCl(cat)_2(OH)^-$.[19]

The compound $[N(n\text{-}C_5H_{11})_4][PCl_2(cat)_2]$ was prepared in solution by addition of excess of $[N(n\text{-}C_5H_{11})_4]Cl$ to a solution of $PCl(cat)_2$ in CH_2Cl_2. The shift observed (−61.3 p.p.m.) was slightly lower than the limiting shift of −66.2 p.p.m., but indicated that more than an equimolar amount of chloride had been added.[6] Addition of $Li[N_3]$ to this solution caused the appearance of ^{31}P n.m.r. signals at −27.5, −82.2, and −111.3 p.p.m., readily assigned to $P(N_3)(cat)_2$, $PCl(cat)_2(OH)^-$, and $PCl(N_3)(cat)_2^-$ respectively. The reaction could be driven no further by addition of an excess of azide, and there was no evidence for formation of the fully substituted species $P(N_3)_2(cat)_2^-$.

Violent reaction, with evolution of N_2, occurred when $Li[N_3]$ was added to a solution of $PCl_3(cat)$ in $PhNO_2$. The ^{31}P n.m.r. spectrum clearly showed the presence of $PCl(cat)_2$ (−8.9 p.p.m.), $(NPCl_2)_3$ (21.1 p.p.m.), $[NP(N_3)_2]_3$ (11.4 p.p.m.), and $(NPCl_2)_4$ (−5.8 p.p.m.), together with an unassigned resonance at 3.5 p.p.m. No peaks attributable to direct substitution products of $PCl_3(cat)$ were observed. Addition of a small amount of $Li[N_3]$ to a solution of $PCl_3(cat)$ in CH_2Cl_2 caused effervescence, the ^{31}P n.m.r. spectrum showing, in addition to starting material, $PCl(cat)_2$ and resonances at 4.9 and −35.5 p.p.m. The last rapidly disappeared and signals due to $(NPCl_2)_3$ and $[NP(N_3)_2]_3$ became apparent. To confirm the identity of $PCl(cat)_2$, which gives a resonance close to that of $[NP(N_3)_2]_4$, the solution was treated with more $Li[N_3]$, causing the expected resonance at −26.7 p.p.m. from $P(N_3)(cat)_2$ to appear. The results thus suggest that the main route for decomposition of $PCl_{3-n}(N_3)_n(cat)$ is *via* disproportionation to bis(catechyl) compounds and (presumably) $PCl_{5-n}(N_3)_n$ species, which rapidly decompose to phosphazenes. The initial peak at −35.5 p.p.m. in CH_2Cl_2 could arise from a molecular species such as $PCl_2(N_3)(cat)$, in accordance with its subsequent rapid disappearance. The signals at 3.5 p.p.m. ($PhNO_2$) and 4.9 p.p.m. (CH_2Cl_2) could be due to $[NP(cat)]_3$,[20] for which no n.m.r. data appear to have been reported, although the shifts are similar to those of $[NP(OEt)_2]_3$ at −0.6 p.p.m.[21] and $[NP(OPh)_2]_3$ at 9.0 p.p.m.[22] This was only a minor product, however.



SCHEME 2

A solution of $[N(n\text{-}C_5H_{11})_4][PCl_4(cat)]$ was prepared by addition of $[N(n\text{-}C_5H_{11})_4]Cl$ to $PCl_3(cat)$ in CH_2Cl_2 until the limiting shift of −156.1 p.p.m.[6] was reached. Reaction with successive small quantities of $Li[N_3]$ caused the appearance of new resonances and allowed the pattern of substitution to be established, as shown in Table 3. Observation of the $PCl(N_3)_3(cat)^-$ ion was always difficult since it appeared to be very activated towards further substitution, and its presence in solution was transient. The fully substituted ion $P(N_3)_4(cat)^-$ appeared to be indefinitely stable in solution, similar to the high kinetic stability of the $P(N_3)_6^-$ ion.[5,13] The lower members of the series decomposed only slowly, in contrast to the $PCl_{6-n}(N_3)_n^-$ series for $1 \leqslant n \leqslant 4$,[13] the decomposition products being identified as phosphonitrilic chlorides and azides (mainly trimers and tetramers), and $P(N_3)(cat)_2$. A low concentration of $PCl(N_3)(cat)_2^-$ was also detected. A plausible mechanism for the decomposition is illustrated for $PCl_3(N_3)(cat)^-$ in Scheme 2. The presence of an excess of Cl^- suppresses step (i), accounting satisfactorily for the small extent of decomposition. The high kinetic stability of $P(N_3)_4(cat)^-$ presumably arises because its only feasible route of decomposition would involve loss of N_3^- to give a particularly unstable molecular species.

TABLE 3

$\delta(^{31}P)$ (p.p.m.) for $PCl_{4-n}(N_3)_n^-(cat)$ in CH_2Cl_2

n	0	1	2	3	4
δ	−156.7	−130.6	−117.9	−122.2	−143.8

Although this system has the possibility of isomerism for $n = 0$—3, only four new resonances were seen, implying either that one isomer of each ion is formed preferentially, or that the shift differences are too small to be resolved. Unfortunately, the method of pairwise interactions cannot be applied in this instance because of the many unknown terms, such as the ' internal ' O : O term from the catechyl group. [This term could be evaluated only if the configuration of the ion $PCl_2(cat)_2^-$ was known.]

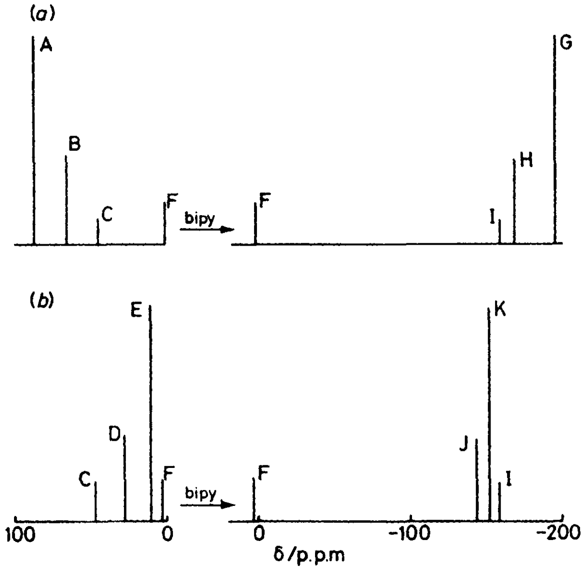
Azido-derivatives of $PRCl_3^+$ *Cations* (R = Me *or* Ph).—The compounds $[PMeCl_3][SbCl_6]$[9] and $[PPhCl_3][BCl_4]$[8] when treated with $Li[N_3]$ in $MeNO_2$ solution showed resonances upfield from the starting material, readily assignable to azido-substituted cations as shown in Table 4. The shift values for the fully substituted species $PR(N_3)_3^+$ are in good agreement with those obtained by Schmidt and co-workers.[3,4]

TABLE 4

$\delta(^{31}P)$ (p.p.m.) for $PRCl_{3-n}(N_3)_n^+$ in CH_3NO_2

n	0	1	2	3
R = Me	120.9	90.4	67.8	51.6
R = Ph	101.6	72.6	51.6	37.1

Azido-derivatives of $[PCl_4(bipy)][SbCl_6]$.—A solution of $[PCl_4(bipy)][SbCl_6]$ (bipy = 2,2′-bipyridyl) in $MeNO_2$ did not react with $Li[N_3]$, and the only resonance seen was at −192.6 p.p.m., due to the cation.[7] When 2,2′-bipyridyl was added to a solution containing the ions $PCl_{4-n}(N_3)_n^+$,[5] however, new resonances appeared in the six-co-ordinate region of the spectrum. A solution containing predominantly PCl_4^+ and $PCl_3(N_3)^+$ gave rise to a spectrum containing a signal due to $PCl_4(bipy)^+$, together with lower-field resonances, as shown schematically in the Figure. When the more highly azido-substituted cations were similarly treated new resonances at slightly lower field in the six-co-ordinate region were seen (Figure). Structures were assigned to the various species by comparison of the intensities of the known cation signals with those in the six-co-ordinate region, and the shifts are given in Table 5. The complexes showed no sign of decomposition over a period of a few hours. The signal at 11.4 p.p.m. disappeared completely on addition of 2,2'-bipyridyl, implying that little or no decomposition of the azidochloro-cations to $[NP(N_3)_2]_3$ had occurred at this stage, and that this resonance was due solely to $P(N_3)_4^+$.[4,5] As in the monocatechyl system, isomerism is possible in this series for n = **1—3**, but a particular isomer of each ion may well be formed preferentially. There are again too many unknown terms to permit the use of the method of pairwise interactions for assigning configurations.



Schematic representation of the effect on the ^{31}P n.m.r. spectrum of adding bipy to $PCl_{4-n}(N_3)_n^+$ species: (*a*) $0 \leqslant n \leqslant 2$; (*b*) $2 \leqslant n \leqslant 4$; peaks are due to PCl_4^+ (A), $PCl_3(N_3)^+$ (B), $PCl_2(N_3)_2^+$ (C), $PCl(N_3)_3^+$ (D), $P(N_3)_4^+$ (E), PCl_3O (F), $PCl_4(bipy)^+$ (G), $PCl_3(N_3)(bipy)^+$ (H), $PCl_2(N_3)_2(bipy)^+$ (I), $PCl(N_3)_3(bipy)^+$ (J), and $P(N_3)_4(bipy)^+$ (K)

TABLE 5

$\delta(^{31}P)$ (p.p.m.) for $PCl_{4-n}(N_3)_n(bipy)^+$ in CH_3NO_2

n	0	1	2	3	4
δ	−192.6	−166.9	−156.9	−142.7	−150.9

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REFERENCES

[1] E. Fluck, *Top. Phosphorus Chem.*, 1967, **4**, 291.
[2] R. J. W. Cremlyn and D. H. Wakeford, *Top. Phosphorus Chem.*, 1976, **8**, 1.
[3] A. Schmidt, *Chem. Ber.*, 1970, **103**, 3923.
[4] W. Buder and A. Schmidt, *Chem. Ber.*, 1973, **106**, 3812.
[5] K. B. Dillon, A. W. G. Platt, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1980, 1036.
[6] K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1978, 1465.
[7] K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1977, 1410.
[8] K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1978, 1318.
[9] R. M. K. Deng, K. B. Dillon, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, to be submitted.
[10] N. Hoffman-Bang, *Acta Chem. Scand.*, 1957, **11**, 581.
[11] K. B. Dillon, M. P. Nisbet, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1978, 1455.
[12] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 1967, **5**, 227.
[13] K. B. Dillon, A. W. G. Platt, and T. C. Waddington, *J. Chem. Soc., Chem. Commun.*, 1979, 889.
[14] P. Volgnandt and A. Schmidt, *Z. Anorg. Allg. Chem.*, 1976, **425**, 189.
[15] T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, 1967, **46**, 1830.
[16] J. S. Hartman and J. M. Miller, *Inorg. Chem.*, 1974, **13**, 1467.
[17] K. B. Dillon and J. M. Miller, unpublished work.
[18] M. P. Nisbet, Ph.D. Thesis, Durham, 1976.
[19] R. N. Reeve, Ph.D. Thesis, Durham, 1975.
[20] H. R. Allcock, *J. Am. Chem. Soc.*, 1964, **86**, 2591.
[21] M. L. Nielsen, J. V. Pustinger, and J. Strobel, *J. Chem. Eng. Data*, 1964, **9**, 167.
[22] R. B. Clampitt, unpublished results quoted in ref. 12.