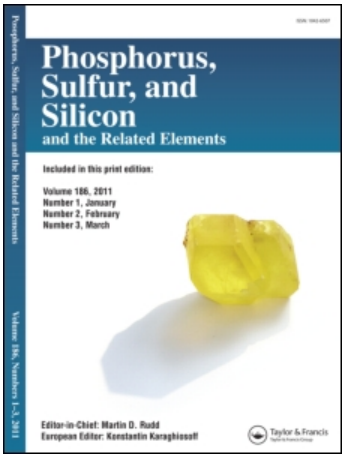


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

AN INVESTIGATION OF THE REACTION PRODUCTS OF $N_3P_3CL_4(NH_2)_2$ WITH NUCLEOPHILIC REAGENTS. EXAMPLES OF GEMINAL → NON-GEMINAL REARRANGEMENTS

John K. Fincham[a]; Michael B. Hursthouse[b]; Harold G. Parkes[a]; Leyl S. Shaw (Née Gözen)[ab]; Robert A. Shaw[a]
[a] Department of Chemistry, Birkbeck College (University of London), London, U.K. [b] Department of Chemistry, Queen Mary College (University of London), London, U.K.

To cite this Article Fincham, John K. , Hursthouse, Michael B. , Parkes, Harold G. , Shaw (Née Gözen), Leyl S. and Shaw, Robert A.(1986) 'AN INVESTIGATION OF THE REACTION PRODUCTS OF $N_3P_3CL_4(NH_2)_2$ WITH NUCLEOPHILIC REAGENTS. EXAMPLES OF GEMINAL → NON-GEMINAL REARRANGEMENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 28: 1, 185 — 194
To link to this Article: DOI: 10.1080/03086648608072808
URL: http://dx.doi.org/10.1080/03086648608072808

Phosphorus and Sulfur, 1986, Vol. 28, pp. 185–194
0308-664X/86/2802-0185/$15.00/0

AN INVESTIGATION OF THE REACTION PRODUCTS OF $N_3P_3CL_4(NH_2)_2$ WITH NUCLEOPHILIC REAGENTS. EXAMPLES OF GEMINAL → NON-GEMINAL REARRANGEMENTS

JOHN K. FINCHAM,[a] MICHAEL B. HURSTHOUSE,[b] HAROLD G. PARKES,[a] LEYLÂ S. SHAW (NÉE GÖZEN)[a,b] and ROBERT A. SHAW[a]*

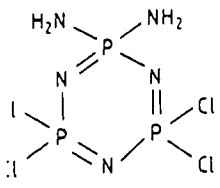
[a]*Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX, U.K.*
[b]*Department of Chemistry, Queen Mary College (University of London), Mile End Road, London E1 4NS, U.K.*

Based on its reactions with various nucleophiles both geminal and non-geminal structures have been earlier proposed for $N_3P_3Cl_4(NH_2)_2$, although its geminal structure is now considered established. The reactions of this compound with alcohols have been investigated and the products examined by NMR spectroscopy and X-ray crystallography. Evidence for both unrearranged as well as geminal → non-geminal rearranged alcoholysis products is presented.

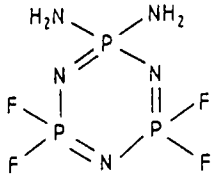
STRUCTURE OF DIAMINOTETRACHLOROCYCLOTRIPHOSPHAZATRIENE, $N_3P_3Cl_4(NH_2)_2$

Although no crystal structure is to date available for $N_3P_3Cl_4(NH_2)_2$ (**1**), much discussion has appeared earlier[1–8] as to whether its structure is geminal or non-geminal. Little doubt now exists about its geminal nature.

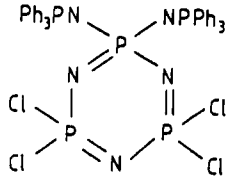
Three derivatives, $N_3P_3(NH_2)_2F_4$,[9] (**2**), $N_3P_3(NPPh_3)_2Cl_4$,[10] (**3**), and $N_3P_3(NH_2)(NPPh_3)Cl_4$,[11] (**4**) have been investigated by X-ray crystallography and were shown to have a geminal disposition of the two nitrogeneous substituents.



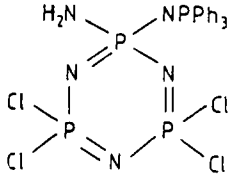
1



2



3



4

The same geminal structure is deduced by ^{31}P NMR spectroscopy for compound (**1**).[5,6,12] Proton coupling is not apparent at room temperature (Figure 1a). At lower temperatures the B part of the A_2B ^{31}P spectrum in acetone at $\delta_B = 8.00$ ppm

*Author to whom all correspondence should be addressed.

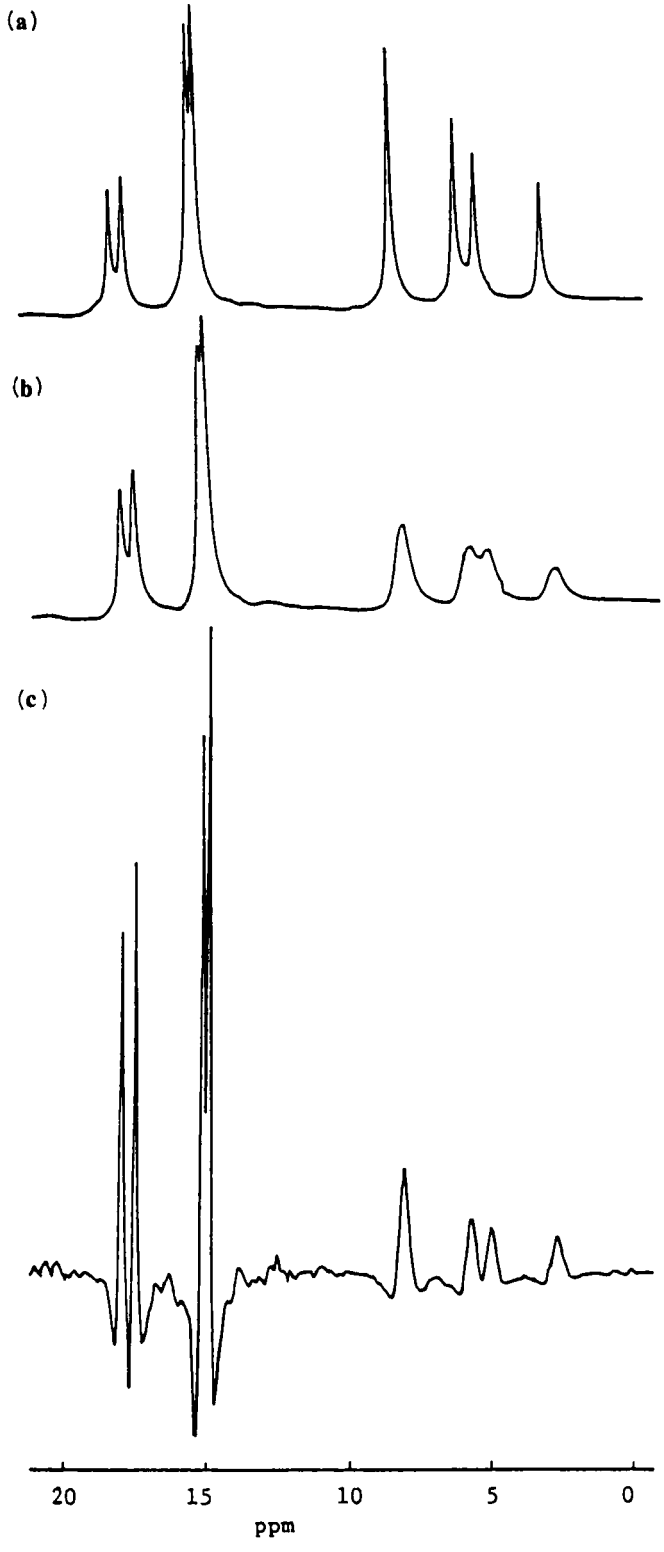


FIGURE 1 The ^{31}P NMR low temperature spectra proton coupled and proton decoupled of compound (**1**).

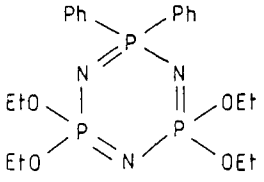
broadens approximately four times in width compared to approximately only one and a quarter times broadening for the A part at $\delta_A = 15.9$ ppm (Figure 1b), resolution enhanced (Figure 1c).

ALCOHOLYSIS REACTIONS

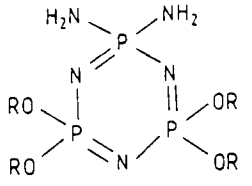
Hexa-alkoxy and hexa-aryloxycyclotriphosphazatrienes have been prepared by the reactions of the appropriate chlorophosphazene either with alkoxide, aryloxide ion, or with an alcohol in the presence of a hydrogen chloride acceptor.[13-15]

The mixed derivatives [$N_3P_3(OR)_nX_{6-n}$, alkoxychloro-,[15-17] aryloxychloro-,[18] alkoxydimethylamino-,[19] aryloxydimethylamino-,[20] aryloxydiamino-,[4,12] alkoxydiphenyl-[21] and alkoxyaminophosphazenyl-[22] derivatives] have been prepared using the appropriate alkoxide or aryloxide ion.

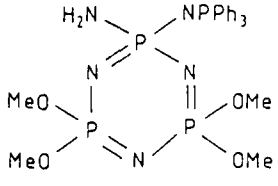
The geminal derivatives $N_3P_3Cl_4X_2$[$X_2 = Ph_2$,[21] $(NH_2)_2$,[4,12] $(NH_2)(NPPh_3)$[22]] have been reported to yield fully alcoholised geminal derivatives (**5**), (**6**) and (**7**), the structures being deduced by ^{31}P NMR spectroscopy. We now report that the alcoholysis of $N_3P_3Cl_4(NH_2)_2$ (**1**) with sodium alkoxides in alcohols yields not only unrearranged, but also rearranged alcoholysis products involving a geminal $P(NH_2)_2$ grouping rearranging to two non-geminal $P(NH_2)(OR)$ groupings.[8]



5



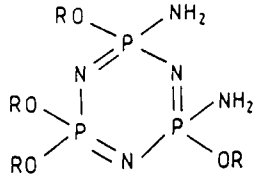
6 R = OC_6H_5, OC_6H_4F-p, OC_6H_4Cl-p, $OC_6H_4CH_3$-p



7

The first reaction to be investigated by us was that of compound (**1**) with sodium *n*-propoxide in *n*-propanol.

The ^1H NMR spectrum ($CDCl_3$) is very complex, showing the presence of two environments. The OCH_2 signals with ^{31}P heteronuclear decoupling of compound (**8**), $N_3P_3(NH_2)_2(OR)_4$ where R = Pr^n is shown in Figure 2. An initial spectrum



8 R = Pr^n, Et, Bu^n

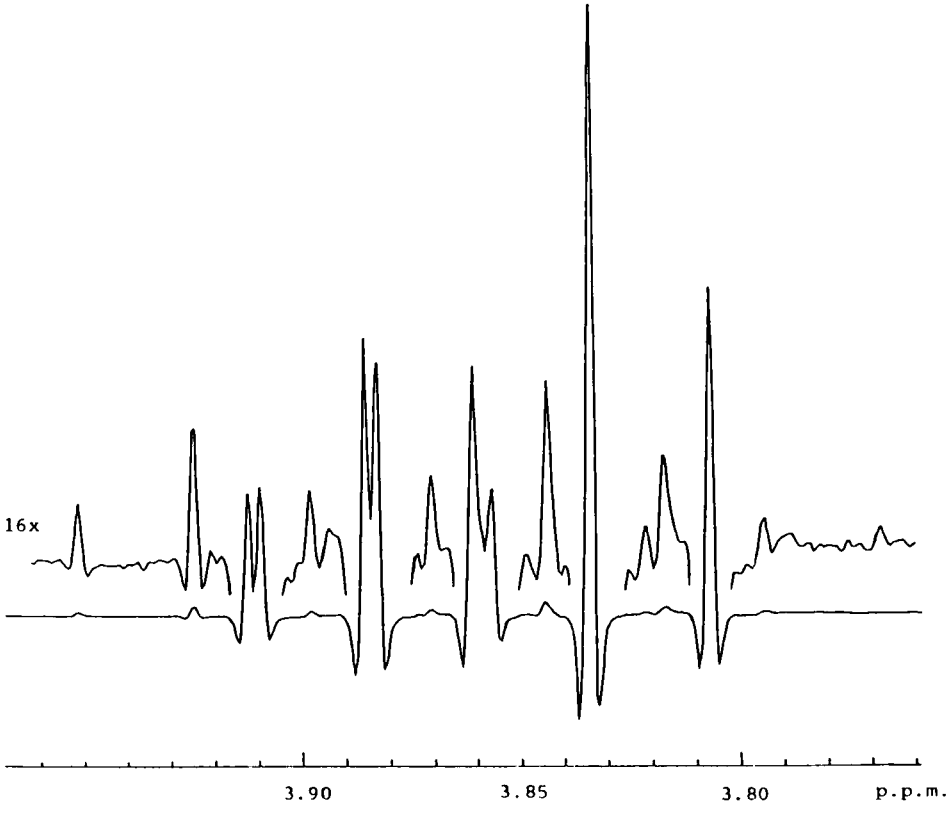


FIGURE 2 The $^1H\{^{31}P\}$ NMR spectrum of compound (**9**) showing the OCH_2 region.

suggested *three environments* (and hence a *cis* structure), but following the X-ray crystallographic structure determination (see below), a longer accumulation time showed low intensity peaks (Figure 2), indicating that the apparent two low-field environments of the OCH_2 groups of the *n*-propoxy groups are the central two lines of an AB quartet, due to intrinsic asymmetry of the OCH_2 protons. Both *n*-propoxy environments $[P(OPr^n)_2]$ and $[P(OPr^n)(NH_2)]$ have this intrinsic asymmetry, but only the one of the former has been observed.

The structure of compound (**8**), $N_3P_3(NH_2)_2(OR)_4$ where $R = Pr^n$ is shown in Figure 3.[8]

Similar NMR data were obtained for ethoxy and *n*-butoxy derivatives indicating that here too *trans* non-geminal structures are the major products. The O → N alkyl group migration in alkoxyphosphazenes to yield oxophosphazanes is well established,[23-30] as are the *cis* ⇌ *trans* rearrangements in non-geminal aminochlorocyclotriphosphazatrienes.[31-35]

The compounds of type (**8**) are the first recorded examples in phosphazene chemistry in which a geminal $P(NH_2)_2$ group rearranges to give two *trans* non-geminal groupings $P(NH_2)(OR)$.

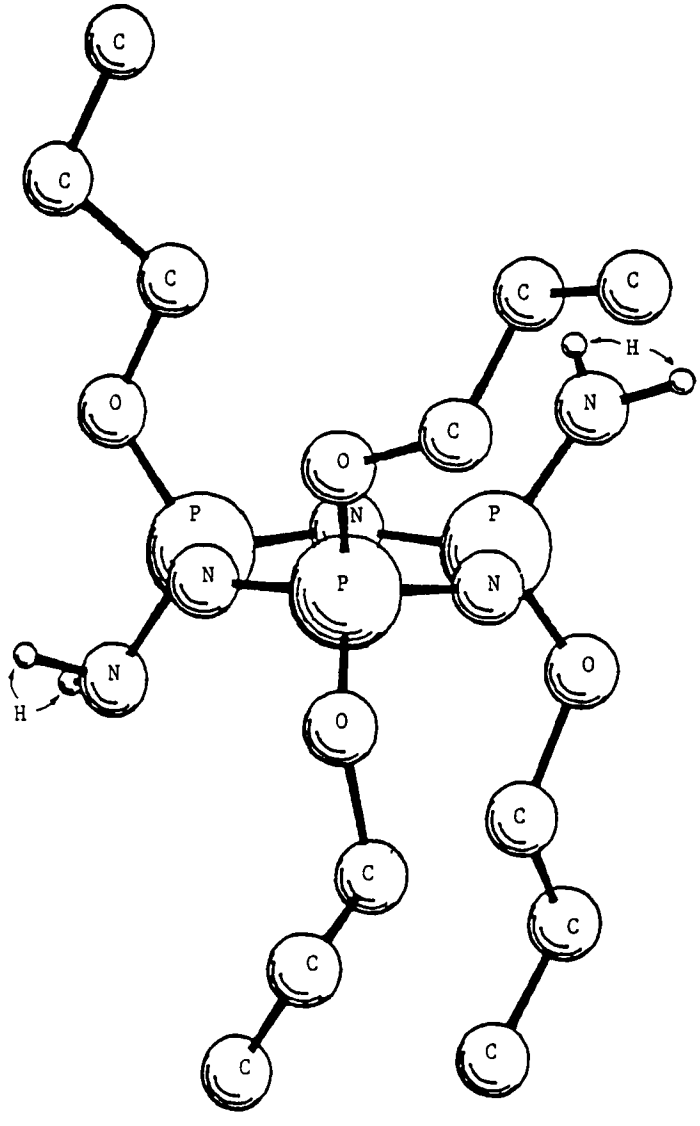


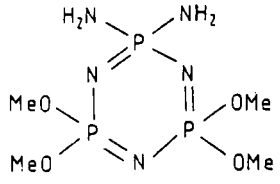
FIGURE 3 The X-ray structure of compound (**8**), R = Pr^n.

TABLE I

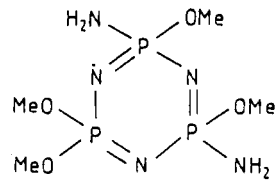
^{31}P NMR Chemical Shifts for $N_3P_3(OR)_4(NH_2)_2$ (**9**)

Compound	$\underline{P}(NH_2)(OR)$ ppm	$\underline{P}(OR)_2$ ppm	^2J(P, P) Hz
R = Et	21.3	16.3	66.7
R = Pr^n	21.4	16.5	66.4
R = Bu^t	21.5	16.5	66.4
$N_3P_3(OEt)_6$	—	14.3	—

Treatment of compound (**1**) with an excess of sodium methoxide gives diaminotetramethoxide derivatives (**9**) and (**10**), $N_3P_3(NH_2)_2(OMe)_4$. We have as yet not observed the *trans* non-geminal derivative, but have obtained crystals which contain two different molecules in a 1 : 1 ratio, one being the *cis* non-geminal derivative and the other being the unrearranged geminal derivatives.



9



10

Its ^{31}P NMR spectrum ($CDCl_3$) is of an A_2B type at room temperature, $\delta_A = 17.9$, $\delta_B = 21.9$ ppm. At lower temperatures in acetone at $-83°C$ two A_2B patterns are observed (Figure 4).

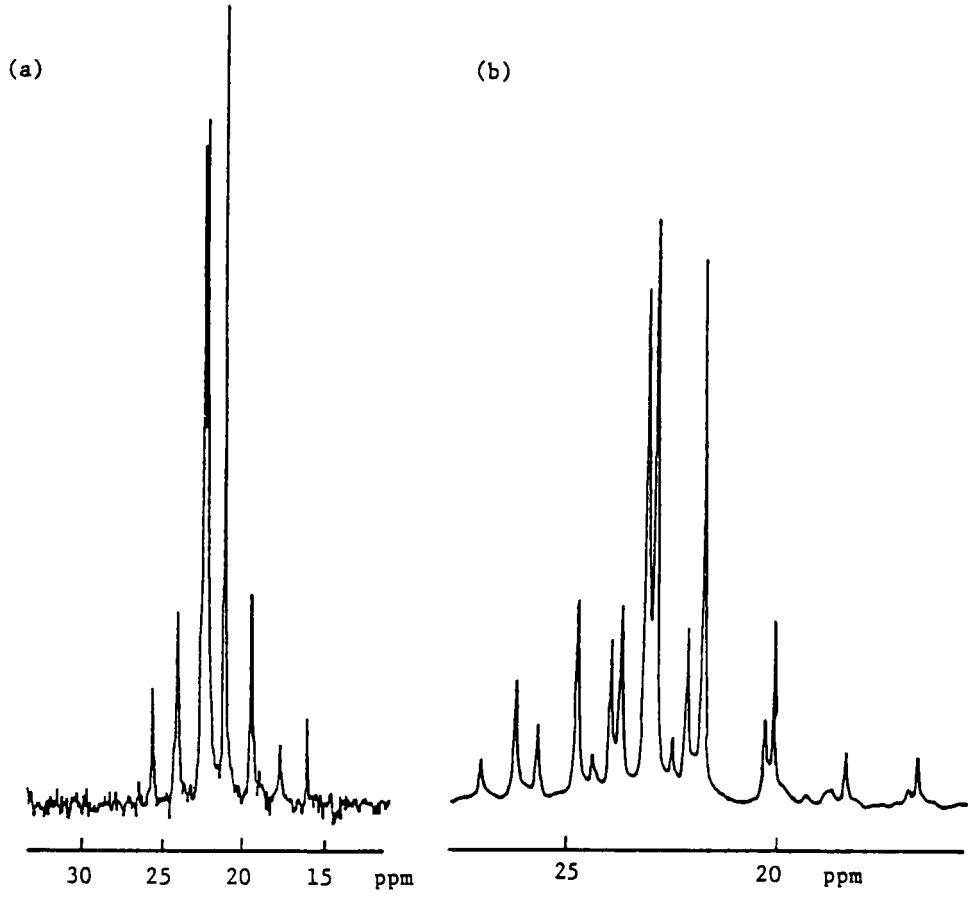


FIGURE 4 The $^{31}P\{^1H\}$ NMR low temperature spectrum of compounds (**9**) and (**10**).

The ^1H NMR spectrum ($CDCl_3$) is complex, but the heteronuclear decoupled spectrum shows the presence of at least four environments.

The ^{13}C NMR spectrum ($CDCl_3$) also is complex, showing the presence of four environments.

The structures of compounds (**9**) and (**10**), $N_3P_3(NH_2)_2(OMe)_4$ are shown in Figure 5.

The compound (**10**) is the first recorded example in phosphazene chemistry in which a geminal $P(NH_2)_2$ group rearranges to give two *cis* nongeminal groupings $P(NH_2)(OMe)$. It also represents a rare, possibly unique, example of two structural isomers being present in the same unit cell.

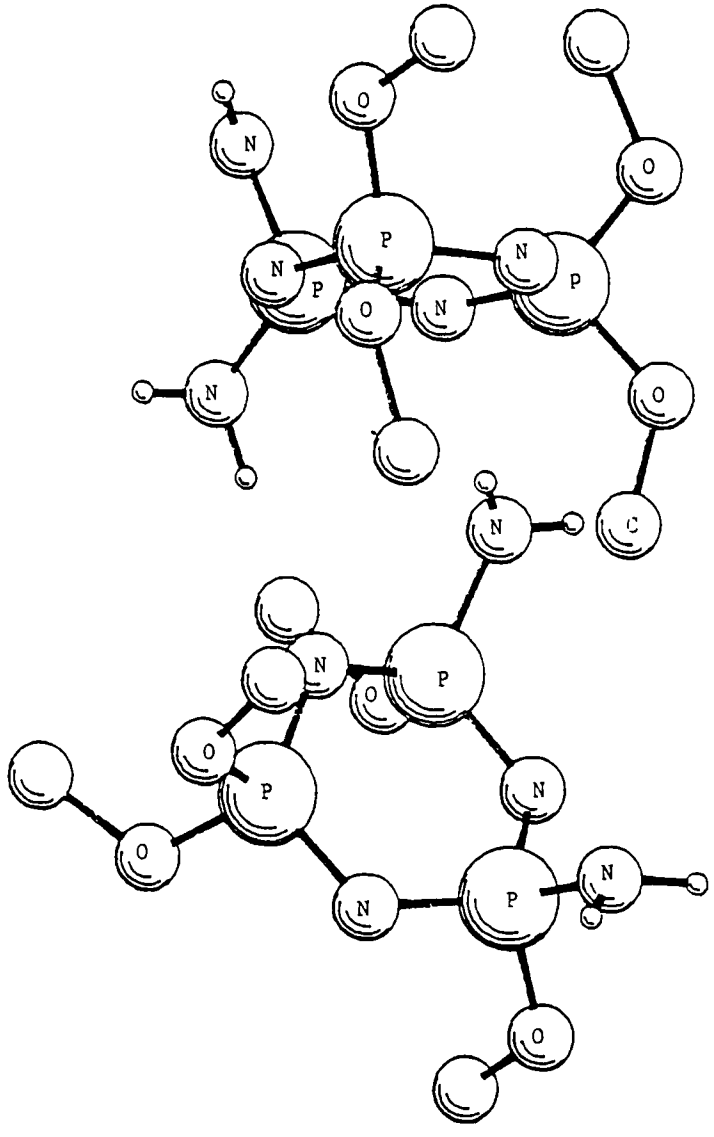
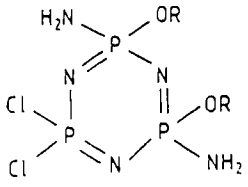


FIGURE 5 The X-ray structure of compounds (**9**) and (**10**).

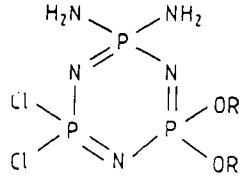
MECHANISM

As the rearranged products have both *cis* and *trans* structures, an intermolecular mechanism seems likely.

Treatment of compound (**1**) with ethanol in the presence of sodium phenoxide and with an excess of sodium isopropoxide gave non-geminal di-isopropoxide and di-ethoxy-diaminodichloro derivatives, $N_3P_3Cl_2(NH_2)_2(OR)_2$ (R = Et, Pr^i). Of the various structural possibilities basicity measurements excluded all except the rearranged (**11**) and unrearranged ones (**12**).[36]



11



12

R = Et or Pr^i

Partial alcoholysis of chlorocyclophosphazenes has so far given almost exclusively non-geminal derivatives with monofunctional alcohols; hence (**12**) is unlikely on chemical grounds. Virtual coupling effects in the ^1H and ^{13}C spectra suggest a non-geminal rearranged structure (**11**), though this does not distinguish between *cis* and *trans* structures. Thus on chemical and NMR grounds, we favour the rearranged structures. We must make a proviso, however, that we were misled into believing that the product $N_3P_3[O(CH_2)_3O][(NHBu^t)_2]Cl_2$[37] had a non-geminal structure from NMR data, due to the accidental isochrony of the $P(NHBu^t)_2$ and the $P[O(CH_2)_3O]$ groupings. X-ray crystallography, however, revealed an unrearranged spiro substituent. We note that diols overwhelmingly prefer gem spiro substitution in contrast to monofunctional alcohols. Hence another accidental isochrony for our partially alcoholised structures seems unlikely (Table II).

The ^{31}P NMR spectra ($CDCl_3$) of $N_3P_3Cl_5(OEt)$,[17] $N_3P_3Cl_5(OPr^i)$,[19] and $N_3P_3Cl_5(NH_2)$[6,7] are included in Table III as a comparison of shift values. At lower temperatures (−85°C) compound (**11**) (R = Pr^i) shows that the A part of the A_2B ^{31}P spectrum in acetone at δ_A = 14.8 ppm broadens, whilst the B part at δ_B = 19.2 ppm is unaffected.

TABLE II

^{31}P NMR data for $N_3P_3Cl_2(OR)_2(NH_2)_2$ (**11**)

Compound	$\underline{P}Cl_2$ ppm	$\underline{P}(NH_2)(OR)$ ppm	$^2J(P,P)$ Hz
R = Et	21.3	15.7	58.6
R = Pr^i	21.1	14.2	58.1

TABLE III

Selected ^{31}P NMR data of Alkoxy and Amino Cyclophosphazenes

Compound	$\underline{P}Cl_2$ ppm	$\underline{P}ClR'$ ppm
$N_3P_3Cl_5OEt$	21.3	13.6
$N_3P_3Cl_5OPr^i$	21.7	12.6
$N_3P_3Cl_5NH_2$	20.4	19.0

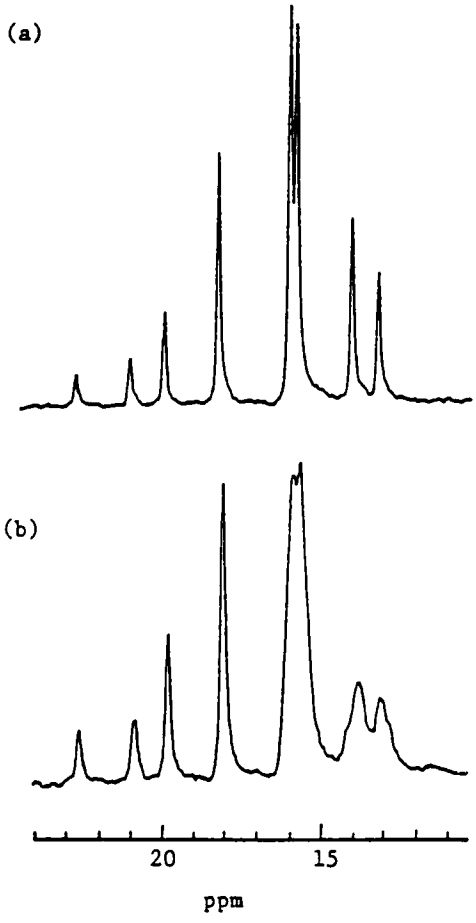


FIGURE 6 The ^{31}P NMR low temperature ^1H decoupled and coupled spectra of compound (**11**), R = Pr^i.

ACKNOWLEDGMENTS

J.K.F. is indebted to I.L.E.A. for same day release. M.B.H. and L.S.S. thank the S.E.R.C. for the provision of crystallographic equipment. R.A.S. is grateful to the Shin Nisso Kako Co. Ltd. for gifts of $N_3P_3Cl_6$, and to the University of London Intercollegiate Research Service for some NMR and mass spectrometric measurements.

REFERENCES

1. M. Becke-Goehring, K. John and E. Fluck, *Z. Anorg. Allg. Chem.*, **302**, 103 (1959).
2. C. T. Ford, F. Dickson and I. Bezman, *Inorg. Chem.*, **3**, 77 (1964).
3. R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), **1966**, 908.
4. E. T. McBee, K. Okuhara and C. J. Morton, *Inorg. Chem.*, **5**, 450 (1966).
5. W. Lehr, *Z. Anorg. Allg. Chem.*, **350**, 18 (1967).
6. G. R. Feistel and T. Moeller, *J. Inorg. Nucl. Chem.*, **29**, 2731 (1967).
7. G. R. Feistel and T. Moeller, *Inorg. Synth.*, **14**, 24 (1973).
8. J. K. Fincham, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen) and R. A. Shaw, *J. Chem. Soc. Chem. Commun.*, **1985**, 252.
9. S. Pohl and B. Krebs, *Chem. Ber.*, **109**, 2622 (1976).
10. M. Krishnaiah, H. Manohar, P. Ramabrahmam and L. Ramamurthy, *Z. Naturforsch.*, **36b**, 765 (1981).
11. J. K. Fincham, M. B. Hursthouse, R. Keat, H. G. Parkes, D. S. Rycroft, L. S. Shaw (née Gözen) and R. A. Shaw, this Symposium.
12. M. Kajuwara and Y. Kurachi, *Polyhedra*, **2**, 1211 (1983).
13. B. W. Fitzsimmons and R. A. Shaw, *Chem. and Ind.*, **1961**, 109; *J. Chem. Soc.*, **1964**, 1735.
14. R. A. Shaw, B. W. Fitzsimmons and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).
15. R.A. Shaw, R. Keat and G. Hewlett, Preparative Inorganic Reactions, Vol. 2, Ed. W. L. Jolly, Interscience, New York, 1965, pp. 49–56.
16. D. Dell, B. W. Fitzsimmons, C. Hewlett, K. Hills and R. A. Shaw, unpublished results.
17. F. Heatley and S. M. Todd, *J. Chem. Soc.* (*A*), **1966**, 1152.
18. D. Dell, B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.*, **1965**, 4070.
19. A. Wende and D. Joel, *Z. Chem.*, **3**, 466 (1963).
20. D. Dell, B. W. Fitzsimmons, R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), **1966**, 1680.
21. C. Hewlett and R. A. Shaw, *J. Chem. Soc.* (*A*), **1966**, 56.
22. J. K. Fincham, M. B. Hursthouse, R. Keat, H. G. Parkes, D. S. Rycroft, L. S. Shaw (née Gözen) and R. A. Shaw, this Symposium.
23. B. W. Fitzsimmons and R. A. Shaw, *Proc. Chem. Soc.*, **1961**, 258.
24. B. W. Fitzsimmons, C. Hewlett and R. A. Shaw, *J. Chem. Soc.*, **1964**, 4459.
25. B. W. Fitzsimmons, C. Hewlett and R. A. Shaw, *ibid*, **1965**, 7432.
26. K. S. Dhathathreyan, S. S. Krishnamurthy, R. A. Shaw, A. R. Vasudeva Murthy, and M. Woods, *J. Chem. Soc. Dalton Trans.*, **1981**, 1928.
27. G. B. Ansell and G. J. Bullen, *J. Chem. Soc. Chem. Commun.*, **1965**, 493; *idem*, *J. Chem. Soc.* (*A*), **1968**, 3026.
28. *Idem*, *J. Chem. Soc. Chem. Commun.*, **1966**, 430; *idem*, *J. Chem. Soc.* (*A*), **1971**, 2498.
29. G. J. Bullen, N. L. Paddock and D. J. Patmore, *Acta Cryst.*, **B33**, 1367 (1977).
30. G. J. Bullen, N. L. Paddock, D. J. Patmore and S. J. Williams, *ibid.*, **B37**, 607 (1981).
31. R. Keat and R. A. Shaw, *Chem. and Ind.*, **1964**, 1232; *idem*, *J. Chem. Soc.*, **1965**, 4067.
32. R. Keat, R. A. Shaw and C. Stratton, *J. Chem. Soc.*, **1965**, 2223.
33. F. R. Ahmed and D. R. Pollard, *Acta Cryst.*, **B28**, 3530 (1972).
34. F. R. Ahmed and E. J. Gabe, *ibid.*, **B31**, 1028 (1975).
35. F. R. Ahmed and S. Fortier, *ibid.*, **B36**, 1456 (1980).
36. N. Gündüz, T. Gündüz, E. Kilic, L. S. Shaw (née Gözen), R. A. Shaw and M. Tüzün, this Symposium.
37. W. F. Deutsch, N. Gündüz, M. B. Hursthouse, E. Kilic, H. G. Parkes, L. S. Shaw (née Gözen), R. A. Shaw and M. Tüzün, this Symposium.