Phosphorus–Nitrogen Compounds. Part XXXV.[1] Friedel–Crafts Reactions of Chlorodimethylaminocyclotriphosphazatrienes with Benzene

By **Sunilkumur Das, Robert A. Shaw,* and Barry C. Smith,** Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX

Chlorodimethylaminocyclotriphosphazatrienes, $N_3P_3Cl_{6-n}(NMe_2)_n$ (n = 1,2,2,3,3, and 3) undergo Friedel–Crafts reactions with benzene in the presence of anhydrous aluminium trichloride to give phenyldimethylamino-derivatives, $N_3P_3Ph_mCl_{6-n-m}(NMe_2)_n$, whose structures are established by their ^{1}H n.m.r. spectra. Replacement occurs readily at $\equiv$PCl·NMe$_2$ groups and more slowly at $\equiv$PCl$_2$ groups. The hydrocarbons triphenylmethane and diphenylmethane are minor by-products in these reactions but are the major products isolated from attempted Friedel–Crafts reactions of *cis*-non-geminal-$N_3P_3Cl_2(NMe_2)_4$. The factors governing the positions of phenylation in the cyclotriphosphazatrienes are discussed.

FRIEDEL–CRAFTS reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, in the presence of anhydrous aluminium trichloride were described in Part V.[2] Reactions with benzene give varying proportions of the geminal diphenyl-$N_3P_3Ph_2Cl_4$, geminal tetraphenyl-$N_3P_3Ph_4Cl_2$, and hexaphenyl-$N_3P_3Ph_6$ derivatives.[2,3] Yields can be increased by the addition of triethylamine.[4] It is conceivable that small quantities of other derivatives might be detected by the most modern chromatographic techniques but it is clear that the replacement pattern is predominantly geminal and pairwise. The only product containing an odd number of aryl groups that has been isolated from Friedel–Crafts reactions of the hexachloride is the mono-*p*-chlorophenyl derivative, $N_3P_3(p\text{-}C_6H_4Cl)Cl_5$.[2]

Non-geminal-triphenyltrichlorocyclotriphosphazatrienes, $N_3P_3Ph_3Cl_3$, can be prepared by ammonolysis and cyclisation.[5,6] *trans*-Non-geminal-$N_3P_3Ph_3Cl_3$ reacts with benzene in the presence of aluminium trichloride [7] to give *cis*- and *trans*-non-geminal tetraphenyl derivatives, $N_3P_3Ph_4Cl_2$, and the pentaphenyl derivative, $N_3P_3Ph_5Cl$.

Friedel–Crafts reactions of two aminochlorocyclotriphosphazatrienes have been reported. Non-geminal-$N_3P_3Cl_4(NMe_2)_2$, m.p. 106 °C, reacts with benzene and xylene [8] to give the diaryl derivatives $N_3P_3Ar_2Cl_2(NMe_2)_2$; and non-geminal-$N_3P_3Cl_4(NHMe)_2$, m.p. 99 °C, reacts with benzene [9] to give the phenyl derivatives $N_3P_3PhCl_3(NHMe)_2$ and $N_3P_3Ph_2Cl_2(NHMe)_2$. The replacement of chlorine by aryl occurred invariably at the non-geminal $\equiv$PCl·NR^{1}R^2 groups.

This paper describes Friedel–Crafts reactions with benzene in the presence of anhydrous aluminium trichloride of the following chlorodimethylaminocyclotriphosphazatrienes, $N_3P_3Cl_{6-n}(NMe_2)_n$, whose structures were established by Keat and Shaw: [10] $N_3P_3Cl_5(NMe_2)$ (I), m.p. 12—14 °C; *cis*-non-geminal-$N_3P_3Cl_4(NMe_2)_2$ (II), m.p. 86 °C; *trans*-non-geminal-$N_3P_3Cl_4(NMe_2)_2$ (III), m.p. 103 °C; *cis*-non-geminal-$N_3P_3Cl_3(NMe_2)_3$ (IV), m.p. 152° C; *trans*-non-geminal-$N_3P_3Cl_3(NMe_2)_3$ (V) m.p. 105 °C; geminal-$N_3P_3Cl_3(NMe_2)_3$ (VI), m.p. 71 °C; and *cis*-non-geminal-$N_3P_3Cl_2(NMe_2)_4$ (VII), m.p. 104 °C. The other known chlorodimethylamino-derivatives were available in small quantities only, *viz.*, geminal-$N_3P_3Cl_4(NMe_2)_2$,[10] or isolated subsequently, *viz.*, *trans*-non-geminal-$N_3P_3Cl_2(NMe_2)_4$,[11] and their Friedel–Crafts reactions have not been investigated.

RESULTS

The first six chlorodimethylamino-derivatives, $N_3P_3Cl_{6-n}(NMe_2)_n$ (n = 1,2,2,3,3, and 3) (I)—(VI) (1 mol ratio) react with boiling benzene in the presence of anhydrous aluminium chloride (6 mol ratio) to give phenylated derivatives, $N_3P_3Ph_mCl_{6-n-m}(NMe_2)_n$, the hydrocarbon triphenylmethane (<3% based on mole phosphazene), and traces of diphenylmethane. The quantity of hydrocarbons increases with the number of dimethylamino-groups in the phosphazene. *cis*-Non-geminal-$N_3P_3Cl_2(NMe_2)_4$ (VII) gave a significant increase in hydrocarbon formation (*ca.* 33% based on mole phosphazene) and no new phosphazene or phosphorus-containing species was isolated.

The starting materials (I)—(VII) and the phosphazenes obtained on phenylation and in some cases on further treatment with dimethylamine, are shown diagrammatically in the Scheme. The structures are deduced from the methods of preparation and the dimethylamino-^{1}H n.m.r. spectra, and are consistent with basicity measurements [12] when available. The m.p.s (or b.p.s) of the products are listed in Table 1.

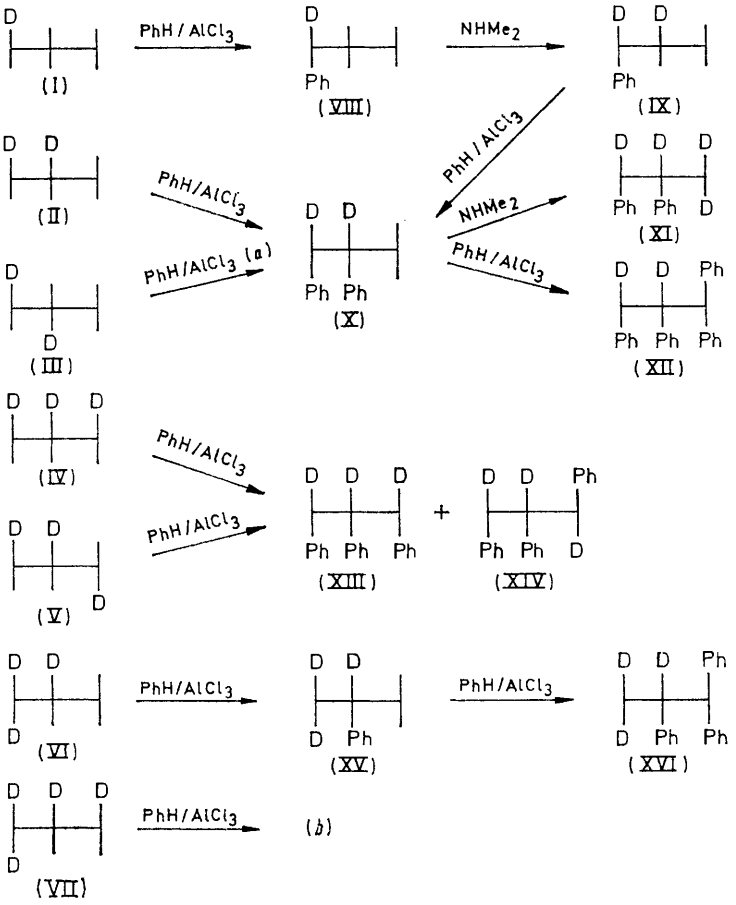
Dimethylamino-^{1}H *N.m.r. Spectra.*—The signals from dimethylamino-protons appear as doublets because of coupling with nearby phosphorus. In some compounds long-range virtual coupling with far phosphorus atoms is indicated by a broad hump between the two strong lines. Chemical shifts and apparent coupling constants for the phenyldimethylaminocyclotriphosphazatrienes are also recorded in Table 1.

[1] Part XXXIV, R. N. Das, R. A. Shaw, B. C. Smith, and M. Woods, *J.C.S. Dalton*, 1973, 709.
[2] K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J. Chem. Soc.*, 1964, 451.
[3] H. Bode and H. Bach, *Ber.*, 1942, **75**, *B*, 215.
[4] E. T. McBee, K. Okuhara, and C. J. Morton, *Inorg. Chem.*, 1965, **4**, 1672.
[5] C. Stratton and R. A. Shaw, *J. Chem. Soc.*, 1962, 5004.
[6] B. Grushkin, M. G. Sanchez, and R. G. Rice, *Inorg. Chem.*, 1964, **3**, 623.
[7] B. Grushkin, M. G. Sanchez, M. V. Ernest, J. L. McClanhan, G. E. Ashby, and R. G. Rice, *Inorg. Chem.*, 1965, **4**, 1538.
[8] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 177.
[9] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1965, **4**, 890.
[10] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.
[11] B. Green and D. B. Sowerby, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3687.
[12] D. Feakins, S. N. Nabi, R. A. Shaw, and P. Watson, *J. Chem. Soc.* (*A*), 1968, 10; D. Feakins, R. A. Shaw, P. Watson, and S. N. Nabi, *J. Chem. Soc.* (*A*), 1969, 2468.

The apparent coupling constants in chlorodimethylaminocyclotriphosphazatrienes (I)—(VII) are greater for ≡PCl·NMe_2, ($^3J^*_{P-H}$ 16·6—17·6 Hz) than for ≡$P(NMe_2)_2$ groups ($^3J^*_{P-H}$ 11·2—12·8 Hz).[13] The apparent coupling constants in phenylchlorodimethylaminocyclotriphosphazatrienes (VIII)—(XVI) are greater for ≡PCl·NMe_2 ($^3J^*_{P-H} > 17$ Hz) than for either ≡PPh·NMe_2 or ≡$P(NMe_2)_2$ groups ($^3J^*_{P-H}$ 11·5—15·2 Hz).

The chemical shifts of $-NMe_2$ protons in chlorodimethylaminocyclotriphosphazatrienes increase with the number of dimethylamino-groups,[13] and in phenyldimethylamino-derivatives with the number of *cis*-phenyl-groups. This is illustrated by the change in chemical shifts along the series: $N_3P_3(NMe_2)_6$, τ 7·45; [13] geminal-$N_3P_3Ph_2(NMe_2)_4$, τ 7·48; [14] and geminal-$N_3P_3Ph_4(NMe_2)_2$, τ 7·53.[14] The effect is considerably greater if the phenyl groups in question are part of a ≡PPh·NMe_2 group (rather than a ≡PPh_2 group), as illustrated by the chemical shifts of the dimethylamino-protons in the isomers, $N_3P_3Ph_3(NMe_2)_3$ (XIII) and (XIV), whose structures are established unambiguously by their

SCHEME Friedel–Crafts reactions of dimethylaminocyclotriphosphazatrienes



D represents $-(NMe_2)$. Cl atoms are omitted. (*a*) Some isomer (II) recovered. (*b*) Phosphazenes not detected.

TABLE 1

Phenyldimethylaminocyclotriphosphazatrienes and their dimethylamino-^{1}H-n.m.r. data

	Compound	M.p. (b.p.)	Structure	τ			J^*_{P-H}/Hz		
(VIII)	$N_3P_3PhCl_4(NMe_2)$	(130 °C/0·01 mmHg)	2:4,4,6,6:2	7·26			15·2		
(IX)	$N_3P_3PhCl_3(NMe_2)_2$	(150 °C/0·01 mmHg)	2:*cis*-4,6,6:2,4	7·29	7·34		17·2	15·0	
(X)	$N_3P_3Ph_2Cl_2(NMe_2)_2$	98 [a]	2-*cis*-4:6,6:2,4	7·34			13·9		
(XI)	$N_3P_3Ph_2(NMe_2)_4$	86 [b]	2-*cis*-4:2,4,6,6	7·32	7·44	7·74	12·0	11·6	11·5
(XII)	$N_3P_3Ph_4(NMe_2)_2$	122 [c]	2,2,4-*cis*-6:4,6	7·46			12·6		
(XIII)	$N_3P_3Ph_3(NMe_2)_3$	115 [d]	2-*cis*-4-*cis*-6:2,4,6	7·40			12·2		
(XIV)	$N_3P_3Ph_3(NMe_2)_3$	95 [e]	2-*cis*-4-*trans*-6:2,4,6	7·53	7·74		12·8	12·9	
(XV)	$N_3P_3PhCl_2(NMe_2)_3$	60	2:4,4:2,6,6	7·35	7·48	7·63	12·6	13·5	13·0
(XVI)	$N_3P_3Ph_3(NMe_2)_3$	108	2,2,4:4,6,6	7·42	7·51	7·65	12·1	12·4	12·3

[a] Lit.,[8] m.p. 99 °C. [b] Lit.,[8] m.p. 83—86 °C. [c] Lit.,[7] m.p. 123—124 °C. Note new configurational assignment. [d] Lit.,[7] m.p. 113·5—115 °C. [e] Lit.,[7] m.p. 93·5—94·5 °C.

[13] R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 1965, 7193.

[14] V. B. Desai, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* (*A*), 1969, 1977.

^{1}H n.m.r. spectra (see below). Similar shielding of dimethylamino-protons is provided by phenoxy- [15] but not by anilino-groups.[14]

$N_3P_3Ph_3(NMe_2)_3$ (XIII) *and* (XIV). *cis*-Non-geminal- (XIII) and *trans*-non geminal-$N_3P_3Ph_3(NMe_2)_3$ (XIV) are both formed by the Friedel–Crafts phenylation of either *cis*-non-geminal- (IV) or *trans*-non-geminal-$N_3P_3Cl_3(NMe_2)_3$ (V). The spectrum of the *cis*-derivative (XIII) consists of one doublet at τ 7·40. The spectrum of the *trans*-derivative (XIV) consists of doublets at τ 7·53 and 7·74 of relative intensities 2 : 1. The chemical shifts of dimethylamino-protons in non-geminal triphenoxytrisdimethylaminocyclotriphosphazatrienes increase similarly with the number of *cis*-phenoxy-groups: *cis*-non-geminal-$N_3P_3(OPh)_3(NM_2)_3$, τ 7·30; *trans*-non-geminal-$N_3P_3(OPh)_3(NMe_2)_3$, τ 7·44 and 7·68 (relative intensities 2 : 1).[15]

Attempts to prepare mono- and di-phenyl derivatives, $N_3P_3PhCl_2(NMe_2)_3$ and $N_3P_3Ph_2Cl(NMe_2)_3$, by this method were unsuccessful. Examination by t.l.c. of the reaction products at 1—2 h intervals showed only the triphenyl derivatives (XIII) and (XIV), starting materials (IV) or (V), and traces of isomerised starting materials.

Both products (XIII) and (XIV) have been prepared previously from reactions of the non-geminal triphenyl derivatives, $N_3P_3Ph_3Cl_3$, with dimethylamine. Their configurations were assigned correctly.[7]

$N_3P_3PhCl_4(NMe_2)$ (VIII). The phenylation of $N_3P_3Cl_5{\cdot}NMe_2$ (I) gives $N_3P_3PhCl_4{\cdot}NMe_2$ (VIII), whose dimethylamino-^{1}H n.m.r. spectrum shows a low-field doublet with split peaks. The apparent coupling constant is below the range found for $\equiv PCl{\cdot}NMe_2$ groups and confirms that the $\equiv PPh{\cdot}NMe_2$ group must be present.

$N_3P_3PhCl_3(NMe_2)_2$ (IX). Reaction of 2:4,4,6,6:2-$N_3P_3PhCl_4{\cdot}NMe_2$ (VIII) with dimethylamine (2 mol. equiv.) in benzene or ether gives $N_3P_3PhCl_3(NMe_2)_2$ (IX). The observed basicity,[12] pK'_a −5·0, confirms the geminal structure. A non-geminal product containing one chlorine attached to each phosphorus could be formed only by migration from the $\equiv PPh{\cdot}NMe_2$ group in (VIII), and would have $pK'_a < -6$.

The dimethylamino-^{1}H n.m.r. spectrum consists of two doublets of equal intensity whose apparent coupling constants are different, and characteristic of $\equiv PCl{\cdot}NMe_2$ and $\equiv PPh{\cdot}NMe_2$ groups. The *cis*-configuration of the two dimethylamino-groups is established by their chemical shifts. Protons in the $\equiv PPh{\cdot}NMe_2$ group, τ 7·34, are more shielded than in the precursor (VIII), τ 7·26, because of the *cis*-dimethylamino-group. A *trans*-dimethylamino-group would provide considerably less shielding (estimated τ 7·27). Protons in the $\equiv PCl{\cdot}NMe_2$ group, τ 7·29, are shielded by the *cis*-dimethylamino-group, but a *cis*-phenyl group would provide considerably more shielding (estimated τ *ca.* 7·5).

Only one isomer (IX) is obtained, and isomerisation does not occur on treatment with aluminium trichloride or dimethylamine hydrochloride in boiling chloroform. Non-geminal chloro-derivatives containing $\equiv PPhCl$ and $\equiv PCl{\cdot}NR_2$ groups frequently (but not invariably) isomerise under these conditions to give mixtures of *cis*- and *trans*-isomers.[16]

$N_3P_3Ph_2Cl_2(NMe_2)_2$ (X). The phenylation of 2:4,4-*cis*-6:2,6-$N_3P_3PhCl_3(NMe_2)_2$ (IX) gives $N_3P_3Ph_2Cl_2(NMe_2)_2$ (X), which was prepared previously by the phenylation of *trans*-non-geminal-$N_3P_3Cl_4(NMe_2)_2$ (III) (lit.,[8] m.p. 106 °C) to which a *cis*-non-geminal structure had been assigned erroneously.[8] The *trans*-non-geminal structure (III) is consistent with its ^{1}H n.m.r. spectrum [13] and dipole moment.[17]

The phenylation of either *cis*-non-geminal- (II) or *trans*-non-geminal-$N_3P_3Cl_4(NMe_2)_2$ (III) gives the same diphenyl derivative (X), and some unchanged *cis*-non-geminal-$N_3P_3Cl_4(NMe_2)_2$ (II) is recovered from both these reactions. The attempted preparation of a monophenyl derivative, *e.g.* (IX) or its isomer, from *trans*-non-geminal-$N_3P_3Cl_4(NMe_2)_2$ (III) was unsuccessful, in contrast to *trans*-non-geminal-$N_3P_3Cl_4(NHMe)_2$.[9]

The diphenyl derivative (X) has the basicity expected for a geminal compound,[12] pK'_a −0·9. The ^{1}H n.m.r. spectrum consists of one doublet whose apparent coupling constant, J^*_{P-H} 13·9 Hz, is characteristic of $\equiv PPh{\cdot}NMe_2$ groups and considerably lower than in isomeric 2,2:4-*trans*-6:4,6-$N_3P_3Ph_2Cl_2(NMe_2)_2$, m.p. 144 °C, $^3J^*_{P-H}$ 17·2 Hz.[14] The *cis*-configuration of the dimethylamino-groups is established from the chemical shift, which is similar to that of the precursor (IX). *cis*-Phenyl groups would provide more shielding (estimated τ *ca.* 7·5).

$N_3P_3Ph_2(NMe_2)_4$ (XI). The reaction of 2-*cis*-4:6,6:2,4-$N_3P_3Ph_2Cl_2(NMe_2)_2$ (X) with an excess of dimethylamine gives $N_3P_3Ph_2(NMe_2)_4$ (XI) which has been prepared previously by this method.[8] The isomerisation of compounds of type (X) has not been observed, and there is no evidence that reaction at $\equiv PCl_2$ is accompanied by inversion at another phosphorus centre. The *cis*-non-geminal structure of $N_3P_3Ph_2(NMe_2)_4$ (XI) is confirmed by the dimethylamino-^{1}H n.m.r. spectrum which consists of three doublets. The protons of the dimethylamino-group flanked by two plenyl groups are the most shielded.

$N_3P_3Ph_4(NMe_2)_2$ (XII). The phenylation of 2-*cis*-4:6,6:2,4-$N_3P_3Ph_2Cl_2(NMe_2)_2$ (X) gives $N_3P_3Ph_4(NMe_2)_2$ (XII), m.p. 122 °C. Grushkin *et al.*[7] reported that *cis*- and *trans*-non-geminal-$N_3P_3Ph_4Cl_2$ react with dimethylamine to give supposed *cis*-non-geminal-$N_3P_3Ph_4(NMe_2)_2$, m.p. 145—145·5 °C, and supposed *trans*-non-geminal-$N_3P_3Ph_4(NMe_2)_2$, m.p. 123—124 °C, which appears identical to (XII). Those configurations were assigned from comparisons of relatively complicated phenyl-^{1}H n.m.r. spectra.[7] Their dimethylamino-spectra consisted of doublets at τ 7·62 and 7·41 respectively, which indicate that the assignments should be reversed, because of the greater shielding by two *cis*-phenyl groups.

The *cis*-non-geminal configuration of the tetraphenyl derivative (XII) is consistent with retention of configuration of the $\equiv PPh{\cdot}NMe_2$ groups in the precursor (X) during reaction at the $\equiv PCl_2$ centre.

$N_3P_3PhCl_2(NMe_2)_3$ (XV). The phenylation of geminal-$N_3P_3Cl_3(NMe_2)_3$ (VI) gives $N_3P_3PhCl_2(NMe_2)_3$ (XV). The basicity,[12] pK'_a −0·1, indicates a geminal structure. The dimethylamino-^{1}H n.m.r. spectrum consists of three doublets of equal intensity whose apparent coupling constants are consistent with the presence of $\equiv PPh{\cdot}NMe$ and $\equiv P(NMe_2)_2$ groups.

$N_3P_3Ph_3(NMe_2)_3$ (XVI). The further phenylation of geminal-$N_3P_3PhCl_2(NMe_2)_3$ (XV) gives $N_3P_3Ph_3(NMe_2)_3$ (XVI), pK'_a +4·7. The geminal structure is confirmed by the dimethylamino-^{1}H n.m.r. spectrum, which consists of three doublets.

[15] D. Dell, B. W. Fitzsimmons, R. Keat, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 1680.

[16] R. Keat, R. A. Shaw, and C. Stratton, *J. Chem. Soc.*, 1965, 2233; R. Keat and R. A. Shaw, *ibid.*, p. 4067.

[17] H. Koopman, F. J. Spruit, F. van Deursen, and J. Bakker, *Rec. Trav. chim.*, 1965, **84**, 341.

DISCUSSION

Earlier work established that the Friedel–Crafts phenylation of hexachlorocyclotriphosphazatriene occurs by a geminal and pairwise replacement pattern.[2-4] Phenyl groups provide greater electron-supply than chlorine, and intermediate ≡PPhCl groups are more susceptible to electrophilic attack by aluminium trichloride than geminal $\equiv PCl_2$ groups. Hence, the second chlorine leaves more easily than the first. Phenylchlorocyclotriphosphazatrienes containing non-geminal ≡PPhCl groups are not intrinsically unstable: non-geminal-$N_3P_3Ph_3Cl_3$, non-geminal-$N_3P_3Ph_4Cl_2$, and $N_3P_3Ph_5Cl$ have all been obtained by other routes;[5-7] but they are not obtained by the Friedel–Crafts phenylation of hexachlorocyclotriphosphazatriene. Only with a more electron-withdrawing substituent than phenyl, *viz.*, *p*-chlorophenyl, has a monoaryl derivative been isolated from a Friedel–Crafts reaction of the hexachloride.[2] Electron-supplying groups, *e.g.*, (di)alkylamino, are expected to lead to rapid phenylation of nongeminal $\equiv PCl{\cdot}NR^1R^2$ groups, and this has been confirmed for a variety of amino-groups.[8,9,18]

This reasoning is supported by independent physical-chemical evidence. Crystallographic investigations of geminal and *cis*-non-geminal-$N_3P_3Cl_3(NMe_2)_3$ by Ahmed and Pollard [19] have shown that non-geminal P–Cl bonds are considerably longer than geminal PCl_2 bonds. Bullen and his co-workers have found similar bond-lengthening in cyclotetraphosphazatetraenes containing non-geminal ≡PPhCl [20] and $\equiv PCl{\cdot}NMe_2$ groups.[21]

A recent study devoted to the ^{35}Cl nuclear quadrupole resonance of some cyclophosphazenes [22] shows that the majority of quadrupole coupling constants for geminal $\equiv PCl_2$ groups fall in the range 26—29 MHz, whereas non-geminal $\equiv PCl{\cdot}NMe_2$ and similar groups in cyclotriphosphazatrienes usually have quadrupole coupling constants <24 MHz. For closely related compounds there is a linear relationship between the P–Cl bond lengths determined by *X*-ray crystallography and the quadrupole coupling constants. The longer bond-lengths and lower quadrupole coupling constants are reasonably identified with greater ionic character.

Thus the factors governing phenylation at a particular phosphorus appear straightforward, but the consequences observed elsewhere in the ring do not. The phenylation of hexachlorocyclotriphosphazatriene does not become faster and smoother with increasing numbers of phenyl groups: when non-geminal ≡PPhCl groups have been phenylated attack at another geminal $\equiv PCl_2$ group is retarded. A similar retardation in the phenylation of non-geminal-$N_3P_3Ph_3Cl_3$ allows the isolation of non-geminal-tetraphenyl and pentaphenyl derivatives.[7] Similarly, stepwise reaction at non-geminal $\equiv PCl{\cdot}NHMe$ groups in the phenylation of non-geminal-$N_3P_3Cl_4(NHMe)_2$ allows a monophenyl as well as the diphenyl derivative to be isolated.[9]

Numerous studies by Feakins, Shaw, and their co-workers [12,23] have shown that phosphazenes develop increasing basicity with increasing numbers of electron-supplying substituents, and that ring-nitrogens are the sites of greatest donor-activity towards protons. This is confirmed by the very accurate *X*-ray crystallographic investigations of geminal-$N_3P_3Cl_2(NHPr^i)_4$,HCl by Mani and Wagner.[24] Adduct formation by nitrogen during the course of a Friedel–Crafts reaction would cause withdrawal of electrons from the P–Cl bond and resultant deactivation. The rate of phenylation thus depends on a balance between opposing effects: *viz.*, complex formation by nitrogen and chlorine. In isomeric geminal and non-geminal derivatives of composition $N_3P_3Cl_4R_2$, where R represents an electron-supplying group relative to chlorine, the nitrogen-donor activity is expected to remain similar, whereas, the chlorine-donor activity would be greater in non-geminal $\equiv PClR$ groups than geminal $\equiv PCl_2$ groups.

Ring-nitrogen atoms are not necessarily donor sites with respect to all Lewis acids and electrophilic reagents. The methylation of aminocyclotriphosphazatrienes can occur at cyclic or exocyclic nitrogen,[25] depending on the substituents. Octakisdimethylaminocyclotetraphosphazatetraene acts as a bidentate σ-ligand through one cyclic and one exocyclic nitrogen to form the adduct $N_4P_4(NMe_2)_8,W(CO)_4$.[26] Solid complexes of hexachlorocyclotriphosphazatriene with aluminium trichloride and aluminium tribromide have been reported.[3,27] *X*-Ray crystallographic data are not available but, as with similar crystalline complexes observed in Friedel–Crafts acylations, the major solid phase, whatever its structure, need not be the most catalytically active. A further complication is that phenylation is enhanced, although not altered, by the presence of triethylamine [4] which probably prevents deactivation of the phosphazene by reducing complex formation with hydrogen chloride and/or aluminium trichloride.

Friedel–Crafts phenylations of dimethylaminocyclotriphosphazatrienes show peculiarities of their own. As expected, non-geminal $\equiv PCl{\cdot}NMe_2$ groups are phenylated in preference to geminal $\equiv PCl_2$ groups. This is illustrated at its simplest by the monodimethylamino- (I) and geminal trisdimethylamino- (VI) derivatives which undergo monophenylation at the non-geminal $PCl{\cdot}NMe_2$

[18] S. K. Das, R. A. Shaw, and B. C. Smith, unpublished results.
[19] F. R. Ahmed and D. R. Pollard, *Acta Cryst.*, 1972, *B*, **28**, 513, 3530.
[20] G. J. Bullen, P. R. Mallinson, and A. H. Burr, *Chem. Comm.*, 1969, 691; G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 1651.
[21] G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 2437; G. J. Bullen, P. E. Dann, V. B. Desai, R. A. Shaw, B. C. Smith, and M. Woods, *Phosphorus*, 1973, **3**, 67.
[22] R. Keat, A. L. Porte, D. A. Tong, and R. A. Shaw, *J.C.S. Dalton*, 1972, 1648, and unpublished results.
[23] D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 1831; D. Feakins, W. A. Last, S. N. Nabi, R. A. Shaw, and P. Watson, *J. Chem. Soc.* (*A*), 1969, 196.
[24] N. V. Mani and A. J. Wagner, *Acta Cryst.*, 1971, *B*, **27**, 51.
[25] J. N. Rapko and G. R. Feistel, *Inorg. Chem.*, 1970, **9**, 1401.
[26] H. P. Calhoun, N. L. Paddock, J. Trotter, and J. N. Wingfield, *Chem. Comm.*, 1972, 875.
[27] G. E. Coxon and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1969, 3012.

group. Non-geminal phenylation occurs also with *cis*-non-geminal (II) and *trans*-non-geminal (III) bisdimethylamino-derivatives. The product from both reactions has a *cis*-non-geminal structure (X), *i.e.*, two dimethylamino-groups are on one side of the ring and two phenyl groups are on the other. In addition, some isomerised *cis*-isomer (II) was obtained from reaction of the *trans*-isomer (III).

Diphenylation of (II) and (III) occurs under all conditions investigated, but a monophenylbisdimethylamino-derivative (IX) is prepared by the dimethylaminolysis of the monophenylmonodimethylamino-derivative (VIII). Thus failure to isolate the monophenyl derivative (IX) during phenylation indicates more rapid reaction than its precursors (II) and (III) rather than inherent instability. The attempted isomerisation of (IX) was unsuccessful under conditions which produce an equilibrium mixture of two isomers for many non-geminal aminochloro-derivatives.[16]

Further investigations of ambident behaviour are in progress.

EXPERIMENTAL

Friedel–Crafts Reactions.—Freshly ground aluminium trichloride (6 mol ratio) was added to the chlorodimethylaminocyclotriphosphazatriene (1 mol ratio) in dry benzene The solution was boiled under reflux (2—6 days), cooled to room temperature, and poured slowly into 2M-hydrochloric acid (*ca.* 150 ml) at 0 °C. The aqueous layer was extracted with benzene (2 × 100 ml), and the combined benzene fractions were washed, dried (Na_2SO_4), decolourised (charcoal), and evaporated to dryness under reduced pressure.

Diphenylmethane and triphenylmethane were detected by t.l.c. using silica gel–light petroleum (b.p. 40—60 °C) and R_f values were compared with those of authentic samples. They were separated from the phosphazenes by elution with light petroleum through a silica gel column. Triphenylmethane (0·01—0·03 mol ratio), m.p. and mixed m.p. 92 °C, was isolated and the i.r. spectrum was compared with that of an authentic sample (Found: C, 93·7; H, 6·7. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%). Traces of diphenylmethane were separated and identified by g.l.c.

Phenyldimethylaminocyclotriphosphazatrienes were separated by elution with light petroleum (b.p. 60—80 °C)–benzene through a silica gel column. Reaction conditions and yields of products are summarised in Table 2. Analytical data are recorded in Table 3.

cis-*Non-geminal*-$N_3P_3Cl_2(NMe_2)_4$.—Anhydrous aluminium trichloride (20·7 g, 0·15 mol) was added to a solution of *cis*-non-geminal dichlorotetrakisdimethylaminocyclotriphosphazatriene 10·0 g, 0·026 mol) in benzene (300 ml) and the

TABLE 2

Preparation of phenyldimethylaminocyclotriphosphazatrienes

Phosphazene	mmol	$AlCl_3$ mmol	PhH ml	Time days		(%)	Products	(%)		(%)
(I)	42	252	300	3	(I)	36	(VIII)	42		
(II)	41	246	350	3	(II)	10	(X)	50		
(III)	32	192	300	3	(III)	16	(II)	8	(X)	41
(IV)	4·7	28	100	2·5	(XIV)	15	(XIII)	25		
(V)	45	270	500	2·5	(XIV)	23	(XIII)	20		
(VI)	53	318	500	2·5	(VI)	12	(XV)	73		
(IX)	18	108	300	2	(IX)	14	(X)	70		
(X)	20	120	300	6	(X)	50	(XII)	10		
(XV)	31	186	300	6	(XV)	44	(XVI)	20		
		$NHMe_2$ mmol	ml	Solvent						
(VIII)	30	62	250	Et_2O	(VIII)	16	(IX)	75		
(X)	3·8	150	100	$CHCl_3$	(XI)	83				

TABLE 3

Analysis of phenyldimethylaminocyclotriphosphazatrienes

		Found (%)					Required (%)			
	Phosphazene	C	H	Cl	N	Formula	C	H	Cl	N
(VIII)	$N_3P_3PhCl_4(NMe_2)$	24·0	3·0	35·5	13·9	$C_8H_{11}Cl_4N_4P_3$	24·1	2·7	35·7	14·0
(IX)	$N_3P_3PhCl_3(NMe_2)_2$	30·0	4·2	25·7		$C_{10}H_{17}Cl_3N_5P_3$	29·5	4·1	26·2	17·2
(X)	$N_3P_3Ph_2Cl_2(NMe_2)_2$	43·2	4·9	15·7	15·5	$C_{16}H_{22}Cl_2N_5P_3$	42·8	4·9	15·8	15·6
(XI)	$N_3P_3Ph_2(NMe_2)_4$	51·4	7·5		21·2	$C_{20}H_{34}N_7P_3$	51·6	7·4	0·0	21·1
(XII)	$N_3P_3Ph_4(NMe_2)_2$	63·4	6·1		13·0	$C_{28}H_{32}N_5P_3$	63·2	6·0	0·0	13·1
(XIII)	$N_3P_3Ph_3(NMe_2)_3$	57·9	6·7		16·7	$C_{24}H_{33}N_6P_3$	57·8	6·7	0·0	16·8
(XIV)	$N_3P_3Ph_3(NMe_2)_3$	57·7	6·5		16·7	$C_{24}H_{33}N_6P_3$	57·8	6·7	0·0	16·8
(XV)	$N_3P_3PhCl_2(NMe_2)_3$	34·6	5·7	16·9	20·0	$C_{12}H_{23}Cl_2N_6P_3$	34·7	5·5	17·1	20·2
(XVI)	$N_3P_3Ph_3(NMe_2)_3$	57·6	7·0		16·8	$C_{24}H_{33}N_6P_3$	57·8	6·7	0·0	16·8

The *cis*-non-geminal (IV) and *trans*-non-geminal (V) trisdimethylamino-derivatives both give rise to two triphenyl derivatives (XIII) and (XIV) and intermediate phenylation products are not obtained. Isomerisation and phenylation may occur by a similar mechanism, but it is not yet known whether aluminium trichloride causes simple polarisation of the P–Cl bond or complete ionisation to form a pseudo-phosphonium ion. In either case, the phosphazene behaves as an ambident electrophile, and the nucleophile benzene can attack at phosphorus or at the α-carbon atom of the dimethylamino-group.

mixture was boiled under reflux (20 h). Separation as before gave crude solid (2·0 g). T.l.c. with silica gel–light petroleum (b.p. 40—60 °C) showed only two products: diphenylmethane and triphenylmethane. Recrystallisation from pentane gave triphenylmethane (1·8 g, 7·7 mmol). A small quantity of diphenylmethane in the mother-liquor was detected by g.l.c. Phosphazenes were not recovered.

A similar reaction of aluminium trichloride and *cis*-non-geminal-$N_3P_3Cl_2(NMe_2)_4$ (2 : 1 mol ratio) in boiling benzene (4 h) gave a mixture of diphenylmethane and triphenylmethane, and unchanged starting material (65%).

Dimethylaminolysis. Details of the reactions of two phenylchlorodimethylaminocyclotriphosphazatrienes with dimethylamine are summarised in Table 2. The general procedures are described elsewhere.[10,13]

We thank the Ministry of Aviation for financial support.

[3/449 *Received*, 28*th February*, 1973]