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ARYLATION REACTIONS OF TRICHLOROPHOSPHAZO-SUBSTITUTED TRIMERIC PHOSPHONITRILIC CHLORIDE

MARLENE KRESGE FELDT and THERALD MOELLER
Noyes Chemical Laboratory, University of Illinois Urbana, Illinois, 61801

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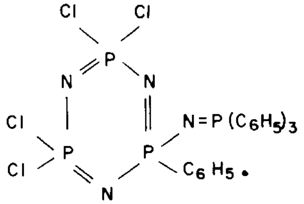
Abstract—Reactions of the trichlorophosphazo derivatives of trimeric phosphonitrilic chloride with aryl Grignard reagents readily yield triarylphosphazo compounds but effect substitution of a ring-bonded chlorine atom only with the compound $N_3P_3Cl_5(N{=}PCl_3)$. The resulting compounds and the related compound $N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$ have been evaluated by infrared and ^{31}P nuclear magnetic resonance spectroscopy. Reaction pattern and nuclear magnetic resonance data for the species $N_3P_3Cl_4Z(N{=}PAr_3)$, $Z{=}Cl$, NH_2, C_6H_5, and $N{=}P(C_6H_5)_3$ indicate 1,1, or geminal, positioning of the $N{=}PAr_3$ and Z groups on the N_3P_3 ring and support earlier conclusions that the compound $N_3P_3Cl_4(NH_2)_2$ has a geminal molecular structure. Chemical shift data are systematized in terms of types of phosphorus-atom environments. A mass-spectrographic fragmentation pattern for the compound $N_3P_3Cl_4[N{=}P(C_6H_5)_3]_2$ indicates clearly the stability of the N_3P_3 heterocyclic arrangement.

INTRODUCTION

ALTHOUGH Rosset reported the preparation of the hexaphenyl derivative by the reaction of trimeric phosphonitrilic chloride with phenylmagnesium bromide[1], a subsequent investigation suggested that ring cleavage occurs, rather than substitution[2]. Methyl[3, 4] and vinyl[3] Grignard reagents are unreactive under comparable conditions, and uncharacterizable oils or solids result with other reagents of this type. The more reactive tetrameric chloride yields with phenylmagnesium bromide two isomeric compounds, $N_4P_4Cl_4(C_6H_5)_4$[5], which have been characterized as the 1,1,5,5-tetraphenyl derivative of the tetramer and the 1-phenyl-1-triphenylphosphazo derivative of the trimer (Formula (*A*))[6]



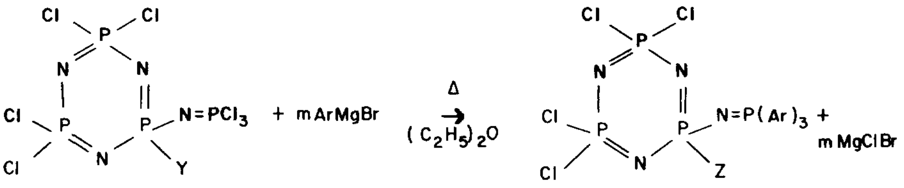
(*A*)

Partial substitution of chlorine atoms in the trimer by strongly electron-repelling groups, however, does enhance reactivity with a Grignard reagent, and the

1. H. Rosset, *C.r. hebd. Séanc. Acad. Sci. Paris* **180**, 750 (1925).
2. H. Bode and H. Bach, *Chem. Ber.* **75**, 215 (1942).
3. G. Tesi and P. J. Slota, Jr., *Proc. chem. Soc.* 404 (1960).
4. M. Yokoyama, *Nippon Kagaku Zasshi* **81**, 1457 (1960).
5. H. Bode and R. Thamer, *Chem. Ber.* **76**, 121 (1943).
6. M. Biddlestone and R. A. Shaw, *Chem. Comm.* 205 (1965).

compounds $N_3P_3[N(CH_3)_2]_3(C_6H_5)_3$, $N_3P_3[N(CH_3)_2]_3(CH_3)_3$, and $N_3P_3[N(CH_3)_2]_3(CH_2{=}CH)_3$ have been so obtained[3].

These observations, plus the successful arylation of the trichlorophosphazo group in linear compounds containing the group $-SO_2-N{=}PCl_3$[7–10], suggested the feasibility of selective substitution of exocyclic chlorine atoms in the geminal compounds $N_3P_3Cl_4(NH_2)(N{=}PCl_3)$ and $N_3P_3Cl_4(N{=}PCl_3)_2$[11, 12] via the Grignard reaction. Specifically, the reactions carried out in terms of the general equation



yielded the products

(II)	$Y = N{=}PCl_3$	$Ar = C_6H_5$	$m = 6$	$Z = N{=}P(C_6H_5)_3$
(III)	$= Cl$	$= C_6H_5$	$= 3$	$= Cl$
(IV)	$= Cl$	$= C_6H_5$	$= 4$	$= C_6H_5$
(V)	$= N{=}PCl_3$	$= p\text{-}C_6H_4CH_3$	$= 6$	$= N{=}P(p\text{-}C_6H_4CH_3)_3$.

For comparison, the compound $Ar{=}C_6H_5$, $Y{=}NH_2$ (VI) was obtained by the reaction of the geminal diamido derivative[11] with triphenyl-phosphorus(V) dibromide[13]. These compounds were characterized in terms of their analyses, physical constants, infrared spectra, and ^{31}P NMR spectra. Additional support for the geminal molecular structural assignment to the compound $N_3P_3Cl_4(NH_2)_2$[11, 12] was provided by the nuclear magnetic resonance data.

EXPERIMENTAL

The common chemicals used were of the best qualities available and were purified and dried by standard procedures. Commerically available trimeric phosphonitrilic chloride was purified by vacuum distillation[11] and repeated crystallization from petroleum ether (b.p. 30–60°). All moisture-sensitive substances were prepared, weighed, or transferred inside a Berkeley-type dry-box.

1,1-Trichlorophosphazo-tetrachloro-cyclotriphosphonitrile, $N_3P_3Cl_4(N{=}PCl_3)_2$ *(compound* (I) *and trichlorophosphazo-pentachloro-cyclotriphosphonitrile,* $N_3P_3Cl_5(N{=}PCl_3)$. These compounds were prepared from the geminal diamido and the monoamido precursors, respectively, as previously described[11].

7. A. V. Kirsanov and Z. D. Nekrasova, *J. gen. Chem. U.S.S.R.* **26**, 1027 (1956).
8. A. F. Vandi and T. Moeller, *Chemy Ind.* 221 (1962).
9. T. Moeller and A. Vandi, *J. org. Chem.* **27**, 3511 (1962).
10. P. Nannelli, A. Failli and T. Moeller, *Inorg. Chem.* **4**, 558 (1965).
11. G. R. Feistel and T. Moeller, *J. inorg. nucl. Chem.* **29**, 2731 (1967); See also G. R. Feistel, *Doctoral Dissertation,* University of Illinois Urbana, Illinois (1965).
12. W. Lehr, *Z. anorg. allgem. Chem.* **350**, 18 (1967).
13. R. Keat, M. C. Miller and R. A. Shaw, *Proc. chem. Soc.* 137 (1964).

1,1-Triphenylphosphazo-tetrachloro-cyclotriphosphonitrile, $N_3P_3Cl_4[N{=}P(C_6H_5)_3]_2$*(II).* A solution of phenylmagnesium bromide, prepared[14] in diethyl ether from 9·55 g (0·06 mole) of bromobenzene and 1·44 g (0·06 mole) of magnesium turnings, was decanted into a three-necked flask equipped with a magnetic stirrer, a pressure-equalizing dropping funnel, and a water-cooled condenser carrying a phosphorus(V) oxide drying tube. To this well-stirred solution, was added, dropwise and over a 2-hr period, 50 ml of a solution of 5 g (0·009 mole) of compound(I) in diethyl ether. The mixture was heated at reflux for 2 hr. The cooled and filtered solution was hydrolyzed by adding it, with stirring, to a mixture of 2N hydrochloric acid and ice, yielding a yellow precipitate. The residue removed from the initial reaction mixture was treated with acetone, and the resulting solution was hydrolyzed similarly to a yellow precipitate. The combined precipitates yielded a fluffy, white, slightly hygroscopic solid (m.p. 198–199°) when recrystallized from ethanol. Yield, *ca.* 27·5 per cent.

Anal. Calc. for $C_{36}H_{30}N_5P_5Cl_4$: C, 52·12; H, 3·62; N, 8·47; Cl, 17·10; mol. wt., 829. Found: C, 52·21; H, 3·87; N, 8·21; Cl, 16·93; mol. wt., 817.

Triphenylphosphazo-pentachloro-cyclotriphosphonitrile, $N_3P_3Cl_5[N{=}P(C_6H_5)_3]$ (III). This compound was prepared essentially as described for compound (II) by the reaction in diethyl ether of phenylmagnesium bromide (from 7·9 g of bromobenzene and 1·2 g of magnesium turnings) with 5 g (0·011 mole) of the compound $N_3P_3Cl_5(N{=}PCl_3)$. The white product, as recrystallized from boiling ethanol, melted at 211–212° (literature[13], 214–215°).

Anal. Calcd. for $C_{18}H_{15}N_4P_4Cl_5$: C, 36·72; H, 2·55. Found: C, 37·13; H, 2·91.

1-Triphenylphosphazo-1-phenyl-tetrachloro-cyclotriphosphonitrile, $N_3P_3Cl_4(C_6H_5)[N{=}P(C_6H_5)_3]$ (IV). A solution of 5 g (0·011 mole) of $N_3P_3Cl_5(N{=}PCl_3)$ in 50 ml of dry diethyl ether was added dropwise over a 2-hr period to a well stirred solution of phenylmagnesium bromide (from 11·8 g of bromobenzene and 1·8 g of magnesium turnings). The reaction mixture was heated at reflux for 4·5–5 hr and then hydrolyzed as described for compound (II). The resulting precipitate was recrystallized from ethanol; m.p., 174–6° (literature[6], 181°); yield, 43 per cent.

Anal. Calc. for $C_{24}H_{20}N_4P_4Cl_4$: C, 45·74; H, 3·18; N, 8·89; Cl, 22·52; mol. wt., 629·7. Found: C, 45·74; H, 3·41; N, 9·03; Cl, 22·18; mol. wt., 622.

1,1-Tri-p-tolylphosphazo-tetrachloro-cyclotriphosphonitrile, $N_3P_3Cl_4[N{=}P(p\text{-}C_6H_4CH_3)_3]_2$ (V). The reaction between compound (I) (3 g, 0·005 mole) and the Grignard reagent (8·7 g of *p*-tolylbromide and 1·23 g of magnesium turnings) was effected as described above, and the mixture was heated at reflux for 2 hr. Hydrolysis of the resulting solution phase yielded a two-layer system, the less dense layer of which gave a yellow solid on being evaporated. The acetone solution obtained by extracting the solid phase from the initial reaction at 0° was hydrolyzed to a second yellow solid. The combined solids were washed quickly with small quantities of benzene until the washings were no longer yellow and then with petroleum ether (b.p. 30–60°). The white solid that formed in the petroleum ether was recovered. A second crop of crystals was obtained by treating the yellow benzene wash liquor with petroleum ether, removing the resulting yellow precipitate, and evaporating the filtrate slowly. Recrystallization of the combined material from boiling ethanol yielded a white solid, m.p. 214–214·5°.

Anal. Calcd. for $C_{42}H_{42}N_5P_5Cl_4$: C, 55·20; H, 4·61; N, 7·68; mol. wt., 913. Found: C, 55·19; H, 4·74; N, 7·54; mol. wt., 916.

1-Triphenylphosphazo-1-amido-tetrachloro-cyclotriphospho-nitrile, $N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$ (VI). This compound was prepared from the compounds $N_3P_3Cl_4(NH_2)_2$ and $(C_6H_5)_3PBr_2$ by an extension of the procedure of Keat, Miller, and Shaw[13].

Instrumental measurements. Phosphorus-31 NMR spectra were obtained with a Varian Model DP-60 instrument equipped with a V-4311 phosphorus probe and operated at 24·288 Mc. A Varian integrator, Model V3521, was used for base-line stabilization. Integrations were effected with a Lasico Planimeter, No. 21160. All samples were measured as 5-ml chloroform solutions in 15-mm o.d. non-spinning tubes and referred to a P_4O_6 external standard. The data were then referred to 85% H_3PO_4. A single spectrum of compound (IV), and referenced directly to 85% H_3PO_4, was obtained at higher resolution by Mr. J. Brautigam of the Monsanto Company. Proton spectra were obtained with a Varian Model A-60A instrument.

Infra-red spectra were measured with a Perkin-Elmer Model 521 grating instrument, using samples in potassium bromide pellets or as Nujol mulls.

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[14] L. F. Fieser, *Organic Experiments*, pp. 90–91. Heath, Boston (1964).

Mass spectra were obtained with an Atlas Model CH4 instrument. Molecular weights were determined osomometrically, using chloroform or carbon tetrachloride solutions.

DISCUSSION

Although substitution of phenyl, and in the one instance investigated, of *p*-tolyl groups for chlorine atoms in the exocyclic —$N{=}PCl_3$ groups proceeds readily, chlorine atoms bonded to ring phosphorus atoms resist very strongly reaction with the Grignard reagents used. The compound $N_3P_3Cl_4(N{=}PCl_3)_2$ is easily converted to the derivatives $N_3P_3Cl_4[N{=}P(C_6H_5)_3]_2$ and $N_3P_3Cl_4[N{=}P(p\text{-}C_6H_4CH_3)_3]_2$, but no additional substitution could be effected irrespective of the rigor of the reaction conditions or the relative stoichiometry of the reactants. Ring substitution did indeed occur in the reaction of phenylmagnesium bromide with the mono-trichlorophosphazo compound $N_3P_3Cl_5(N{=}PCl_3)$, but only after prolonged heating at reflux, and no more than a single ring-bonded chlorine atom could be replaced regardless of the experimental conditions used. Activation of the single chlorine atom by the exocyclic phosphazo group would reasonably be most effective if that chlorine atom and the phosphazo group were bonded to the same ring phosphorus atom. If the substitution involved a non-geminal chlorine atom, all four such atoms could then be involved, with polysubstitution and isomer formation being definitely probable. No evidence for either of these phenomena could be obtained.

This conclusion favors a geminal arrangement of the two trichlorophosphazo groups in the molecule $N_3P_3Cl_4(N{=}PCl_3)_2$, since if these groups were not geminally arranged two activated ring-bonded chlorine atoms should be present, and a product containing two ring-bonded phenyl groups should result. Furthermore, when the diamido compound, $N_3P_3Cl_4(NH_2)_2$, is treated with triphenylphosphorus(V) dibromide, only compound (VI), $N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$, is obtained, even when the triphenylphosphorus dibromide is present in a 4:1 mole ratio. However, when the mole ratio of reactants was increased to 8:1 and the reaction mixture was heated for a longer period of time, compound (II), $N_3P_3Cl_4[N{=}P(C_6H_5)_3]_2$, did result but in only 2 per cent yield (vs. 26 per cent of compound (VI) in the same reaction). These observations support further the conclusion[11, 12] that the parent diamido compound has a geminal molecular configuration, since if the arrangement were really non-geminal, a bis(triphenylphosphazo) product should predominate.

A typical i.r. spectrum (for compound (VI)) is included as Fig. 1. The most significant absorption peaks in the spectra of compounds (II–VI) are given in Table 1. Frequency assignments, based upon an examination of literature data and the measured spectra[15] of the substances 1,1-$N_3P_3Cl_4(C_6H_5)_2$, 1,1-$N_3P_3Cl_4(NH_2)_2$, and $N_3P_3Cl_5(NH_2)$, are listed in Table 2. The spectra of compounds (II), (III), (IV) and (VI) are quite similar, as may be expected. Compound (V), as a consequence of the influence of para-substitution in the phenyl group, gives rise to absorption maxima at higher frequencies. The N_3P_3 ring absorption is broad and strong in all cases except for compound (III), where extensive dilution in the potassium bromide pellet gave more sharply defined absorptions.

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15. M. K. Feldt, Doctoral Dissertation, University of Illinois, Urbaba, Illinois (1967).

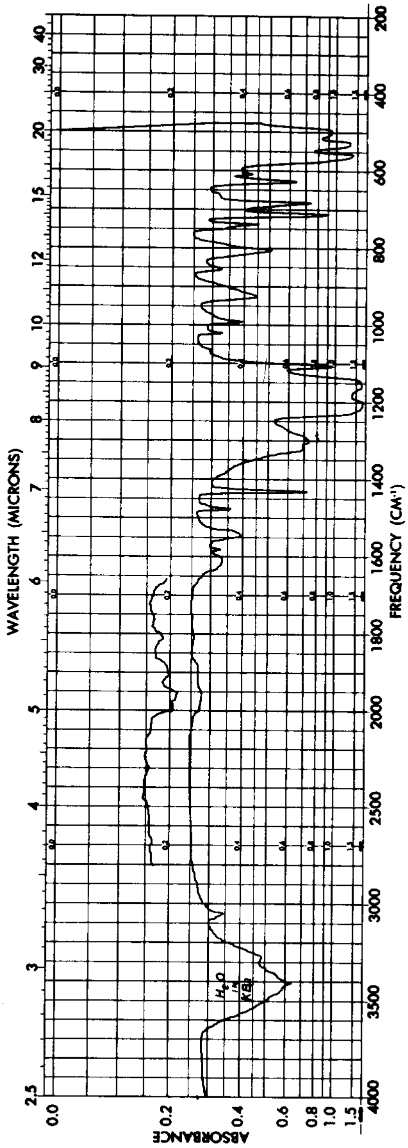


Fig. 1. Infra-red spectrum of the compound $N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$.

Table 1. Infra-red spectra, major bands

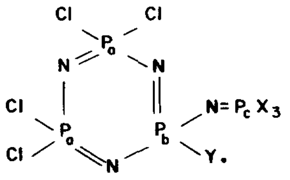
Frequency, cm^{-1}									
Compound (II)*		(III)*		(IV)*		(V)*		(VI)*	
3055(vs)	994(vs)	3055(w)	743(m)	3050(w)	817(s)	3030(s)	1116(s)	3400(vs)	~ 1200(vs)
1957(m)	865(s)	1584(m)	726(s)	1585(vw)	740(s)	2925(s)	1040(m)	3055(w)	~ 1155(vs)
1890(m)	798(vs)	1479(s)	714(s)	1479(m)	717(vs)	2870(m)	1025(s)	2110(m)	1109(m)
1815(m)	736(vs)	1435(vs)	682(vs)	1435(s)	682(vs)	1915(m)	872(s)	2000(m)	1021(w)
1765(m)	710(vs)	~ 1270(s)	643(vs)	~ 1285(s)	635(m)	1603(vs)	832(m)	1957(s)	991(m)
1584(vs)	681(vs)	~ 1180(vs)	574(vs)	~ 1260(s)	575(vs)	1562(m)	805(vs)	1910(s)	925(m)
1568(w)	619(vs)	~ 1108(s)	555(vs)	1025(m)	540(vs)	1503(vs)	711(vs)	1818(m)	855(w)
1478(vs)	609(vs)	1021(m)	512(vs)	995(m)	528(vs)	1450(m)	655(vs)	1665(m)	805(s)
1430(vs)	555(vs)	992(m)	492(s)		507(s)	1401(m)	634(s)	1584(w)	740(s)
1205(vs)	485(vs)	870(m)	448(s)			1380(w)	601(s)	1545(m)	712(s)
1022(vs)	421(m)	850(s)	416(s)			~ 1200(vs)	591(s)	1487(m)	634(s)
		805(m)	400(s)				~ 562(vs)	1432(s)	629(s)
								1300(s)	559(s)
									530(s)

*vs, very strong; s, strong; m, medium; w, weak.

Table 2. Group i.r. frequency assignments

Frequency range, cm^{-1}	Assignment
3200–3400	NH stretch
3045–3055	C_6H_5 (C—H vibration)
1584–1587	C_6H_5 (C=C vibration)
1535–1545	NH deformation
1479–1487	C_6H_5 (C=C vibration)
1430–1435	P—C_6H_5
1100–1300	P—N (ring)
1021–1025	C_6H_5 (C—H vibration)
991–995	C_6H_5 (ring vibration)
925–975	P—NH_2
850–865	PCl_2
710–717	C_6H_5 (C—H deformation)

Each of the compounds investigated has in its structure three phosphorus-atom environments. These may be designated in terms of the general formula



as P_a, ≡ PCl_2; P_b, ≡ $P(Y)(N{=}PX_3)$; and P_c, —$N{=}PX_3$. The ^{31}P NMR spectrum of a typical phosphazo compound (compound (VI)) is included as Fig. 2.

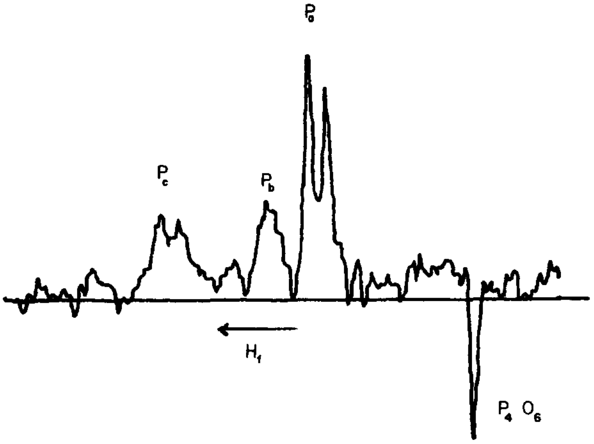


Fig. 2. Tracing of the ^{31}P nuclear magnetic resonance spectrum of the compound $N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$.

Peaks assigned to these types of phosphorus atoms are designated thereon. The spectra of all of the compounds described are similar, although in some cases P_c is a combination of three reproducible individual peaks. The spectra are not subject to first-order interpretation. The assignments P_a, P_b, and P_c were based upon integrated areas, averaged from a number of scans in each instance, and comparisons with the spectra of compounds of known structures. Thus the average area ratios for the spectrum given in Fig. 2 are $a:b:c = 2{\cdot}0:1{\cdot}0:1{\cdot}0$, suggesting the assignment as given. The spectrum of compound (IV) contains only two peaks, the peaks P_a and P_b having chemical shifts that are so nearly the same as to make these two peaks indistinguishable[15]. A more refined measurement of this spectrum showed splitting of the larger peak into a doublet, $J_{P_aP_b} = 23{\cdot}38$ c/s. No other J_{PP} value could be determined from the observed spectra. The presence of three peaks in a 2:1:1 ratio in this spectrum confirmed the location of the ring phenyl group as geminal to the triphenylphosphazo group.

The chemical shifts characteristic of the spectra of compounds (II), (III), (IV) and (VI) together with those of several related compounds, are given in Table 3. The values recorded for compound III are only approximate, as a consequence of its low solubility (ca. 0·21 M) in chloroform. Over the concentration range 0·21–0·56 M, no change in chemical shift was detected for solutions of compound (VI) in chloroform. However, the spectra are somewhat solvent dependent, as was indicated by the fact that for dioxane solutions chemical shifts were ca. 2 p.p.m upfield from those for chloroform solutions.

Substitution of chlorine atoms on the P_c atom by phenyl groups always effects deshielding of this phosphorus atom. The observed shift is ca. 19 c/s. downfield from that reported[11, 12] for the chloro compounds, a value comparable to the downfield shift of 22 p.p.m. observed when phenyl groups are substituted for chlorine atoms in phosphorus(V) oxytrichloride[16]. These effects on chemical

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16. J. H. Letcher and J. R. Van Wazer, *J. chem. Phys.* **44**, 815 (1966).

shifts can be attributed to the presence of ring currents. The orientation of the P_a atom with respect to the phenyl rings will determine the direction of the observed shift. Thus, both the P_b and P_c atoms are deshielded. The effect on the remote P_a atom is strongly dependent upon the nature of the substituents present on the P_b atom. If two phosphazo groups are present, substitution of chlorine by phenyl effects an upfield shift of 4–6 p.p.m. If, however, the P_b atom is monosubstituted, as in the species $N_3P_3Cl_5X$ where X is $—N{=}PCl_3$, $—N{=}P(C_6H_5)_3$, or $—NH_2$, variation of X causes no significant change in the chemical shift characteristic of P_a.

Table 3. Chemical shifts, relative to 85% H_3PO_4, in ^{31}P NMR spectra

Compound	$\equiv PCl_2$	$—N{=}PX_3$*	$\equiv P\begin{matrix} / N^{\dagger} \\ \backslash Y \end{matrix}$
$N_3P_3Cl_4[N{=}P(C_6H_5)_3]_2$(II)‡	−13·4	−5·5	+11·6
$N_3P_3Cl_5[N{=}P(C_6H_5)_3$(III)‡	[−20]¶	[−15]¶	—
$N_3P_3Cl_4(C_6H_5)[N{=}P(C_6H_5)_3]$(IV)‡	−15·8	−2·4	~ −14·6
$N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$(VI)‡	−17·0	−12·1	(+1·8 to +4·1)‖
$N_3P_3Cl_4(NH_2)_2$§	−18·3		−9·03
$N_3P_3Cl_5(NH_2)$§	−20·4		−19·0
$N_3P_3Cl_4[N{=}PCl_3]_2$§	−17·5	+13·5	+20·4
$N_3P_3Cl_5[N{=}PCl_3]$§	−20·5	+3·29	+2·20

*X = Cl, C_6H_5.

†Y = Cl, NH_2, C_6H_5, $NPCl_3$, $NP(C_6H_5)_3$.

‡This investigation.

§Ref. [11].

¶Exact value unobtainable.

‖Broad multiplet.

These results are undoubtedly affected by steric factors. A molecular model suggests that even though two geminally located triphenylphosphazo groups are very bulky they can so fold over as to place the phenyl rings adjacent to the P_a atom. Thus, although on the basis of apparent bond separation the P_a atom and these phenyl groups are widely separated, interactions resulting in the chemical shift ascribed to this phosphorus atom are possible. In the monosubstituted compounds, however, the triphenylphosphazo group is even less constrained. Instead of being somewhat locked into a given configuration, this exocyclic group can move within the limits imposed by its bonds. Inasmuch as smaller repulsions arise when this group is as far from the remaining portions of the molecule as possible, interaction of the phenyl groups with the P_a atom are minimized, and no effect is noted on the chemical shift of this phosphorus atom.

The same effect is observed for linear compounds of the type $Ar_3P{=}N—SO_2Y$[17]. With various Ar groups, when Y is morpholino or dimethyl, diethyl, di-*n*-propyl, or di-*n*-butylamino, the chemical shift of the phosphorus atom is in

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17. T. Moeller and A. Vandi, *J. org. Chem.* **27**, 3511 (1962).

the region −13·6 to −15·8 p.p.m. If, however, Y is —N═PAr$_3$, the observed chemical shift is only ca. −9·8 p.p.m. Again, a molecular model indicates that the phenyl groups can interact with the remote phosphorus atom and thus cause the observed shielding.

The observed chemical shifts also indicate that, as expected, when compounds that can cause ring-current effects are ignored, the change from $\equiv P_b$(—N)(—Cl) to $\equiv P_b$(—N)(—N) causes an upfield shift in the resonance of the P_b atom. As noted from the data summarized in Table 4, there is essentially no change in the shift characteristic of the P_a atom. Here the atoms involved are more than two bonds removed from each other, and no offsetting steric factors are present.

Table 4. Change in chemical shift from $a\equiv$P(—N)(—Cl) to $a\equiv$P(—N)(—N) configuration

Original compound	Final compound	Change in chemical shift for P_a (p.p.m.)
$N_3P_3Cl_5(NH_2)$	$N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$	3·4
$N_3P_3Cl_5(N{=}PCl_3)$	$N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$	3·5
$N_3P_3Cl_5[N{=}P(C_6H_5)_3]$	$N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$	2·8
$N_3P_3Cl_5(N{=}PCl_3)$	$N_3P_3Cl_4(N{=}PCl_3)_2$	3·0
$N_3P_3Cl_5(NH_2)$	$N_3P_3Cl_4(NH_2)_2$	2·1

All of the above assignments and considerations are based upon the assumption of geminal configurations. The spectra of the compounds $N_3P_3Cl_4[N{=}P(C_6H_5)_3]_2$ (II), $N_3P_3Cl_4(NH_2)[N{=}P(C_6H_5)_3]$ (VI), and $N_3P_3Cl_4(C_6H_5)[N{=}P(C_6H_5)_3]$ (IV) can be interpreted to confirm this assumption. The geminal and nongeminal configurations of these molecules, the predicted resonance peaks, and the relative areas under the latter are given in Table 5. Compound (II) should give three resonance peaks irrespective of its molecular configuration, but in a different area ratio. Thus conclusions as to the configuration of this molecular species are not completely definitive. For each of the other two compounds, the geminal arrangement should be characterized by three peaks and the non-geminal by four. Only three peaks are observed experimentally. That the larger peak (P_a) is a real doublet and not a combination of two superimposed peaks of similar chemical shift has been demonstrated by the refined spectrum of compound (IV) which revealed no hidden peaks and indicated that the doublet is a consequence of P_a–P_b coupling. Thus the geminal configurations are the more likely for compounds (IV) and (VI).

The major species identified in the mass-spectral fragmentation pattern of compound (II) are summarized in Table 6. As a consequence of the number of possible fragments and the large number of isotopic nuclides present, the spectrum obtained is highly complex. It is significant both that no peak representing the simple $N_3P_3^+$ entity was observed and thus that the lighter fragments observed are from removal of the exocyclic substituents rather than from ring rupture. The

Table 5. Predictions as to ^{31}P resonance peaks for selected isomers

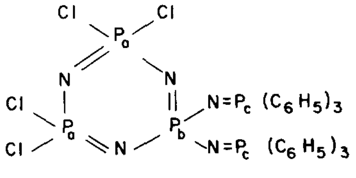
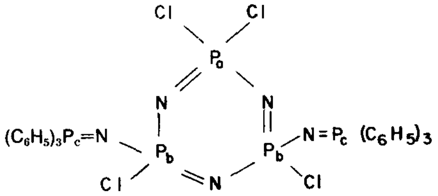
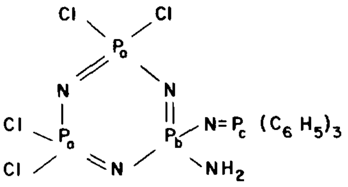
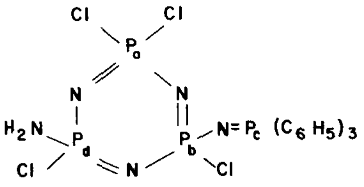
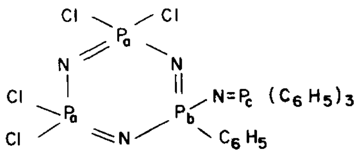
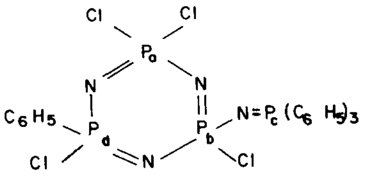
Molecular arrangement	Predicted relative area ratios $P_a : P_b : P_c : P_d$
	2 1 2 0
	1 2 2 0
	2 1 1 0
	1 1 1 1
	2 1 1 0
	1 1 1 1

Table 6. Major species in fragmentation pattern of $N_3P_3Cl_4[N{=}P(C_6H_5)_3]_2$

Mass number	Ion
827	$N_3P_3Cl_4[N{=}P(C_6H_5)_3]_2^+$
792	$N_3P_3Cl_3[N{=}P(C_6H_5)_3]_2^+$
757	$N_3P_3Cl_2[N{=}P(C_6H_5)_3]_2^+$
750	$N_3P_3Cl_4[N{=}P(C_6H_5)_3][N{=}P(C_6H_5)_2]^+$
551	$N_3P_3Cl_4[N{=}P(C_6H_5)_3]^+$
519	$N_3P_3Cl_2[N{=}P(C_6H_5)_3][N{=}P(C_6H_5)]^+$
304	$N_3P_3Cl_4N_2^+$
276	$N{=}P(C_6H_5)_3^+$, $N_3P_3Cl_4^+$
262	$P(C_6H_5)_3^+$
198	$NP(C_6H_5)_2^+$
183	$P(C_6H_5)_2^+$
122	$NP(C_6H_5)^+$
107	$P(C_6H_5)^+$
77	$C_6H_5^+$

N_3P_3 heterocyclic arrangement is apparently highly stable in this compound. These results compare well with those for the mixed chloro-bromo trimers where ca. 70 per cent of the total positive ion intensity is due to fragments containing the N_3P_3 nucleus[18].

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18. G. E. Coxon, T. F. Palmer and D. B. Sowerby, *Inorg. nucl. Chem. Lett.* **2**, 215 (1966).