Geminal Bis[(triphenylphosphoranylidene)amino]cyclotriphosphazenes: Synthesis, Substitution Reactions, and Nuclear Magnetic Resonance Spectra

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Cyclotriphosphazenes bearing an amino ligand are readily converted into the corresponding (triphenylphosphoranylidene)amino ($-N=PPh_3$) derivatives by means of an excess of triphenylphosphine–tetrachloromethane in an acetonitrile–triethylamine medium (Appel reaction). Thus prepared, $N_3P_3Cl_4(N=PPh_3)_2$ reacts with dimethylamine in various solvents according to a geminal substitution pattern; this is an indication of S_N1-type reactions, as a result of the strong electron-donating character of the ligands. The ultimate substitution product $N_3P_3(NMe_2)_4(N=PPh_3)_2$, also prepared from $N_3P_3(NMe_2)_4(NH_2)_2$, is isolated as its HCl or 2HCl adduct, depending on the method of preparation. In both adducts the protons are attached to ring nitrogen atoms, and variable-temperature ^1H and ^{31}P n.m.r. measurements show prototropic behaviour at elevated temperatures. Trends within the ^{31}P n.m.r. parameters of the derivatives are discussed in terms of the electron-donating ability of the ligands.

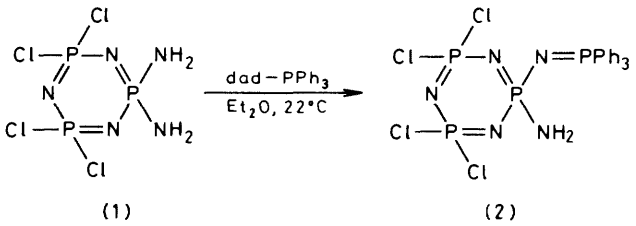
It has been demonstrated by means of various physicochemical methods (*X*-ray diffraction,[1-4] ^{31}P n.m.r. spectroscopy,[5-7] and basicity measurements [6-8]) that (triphenylphosphoranylidene)-amino ($-N=PPh_3$) ligands have a significant influence on the charge distribution within phosphazene ring systems. The electron-donating ability of these ligands is also expected to be reflected in the chemical behaviour of cyclophosphazenes. The monosubstituted derivative of hexachlorocyclotriphosphazene, $N_3P_3Cl_5(N=PPh_3)$, has already been shown to behave rather peculiarly in further nucleophilic displacement reactions,[9] and recently it has been suggested that this might be due to the occurrence of a S_N1-type substitution mechanism.[10]

In this paper, we describe substitution reactions with the geminal-disubstituted derivative 2,2,4,4-tetrachloro-6,6-bis-[(triphenylphosphoranylidene)amino]cyclotri-λ^5-phosphazene, $N_3P_3Cl_4(N=PPh_3)_2$, in which the influence of two strongly electron-donating ligands on the substitution behaviour is anticipated to be marked. To obtain sizeable quantities of this starting material (low-yield preparations of which were already known [11,12]) we designed a novel preparation for it.

Results and Discussion

Preparation of (Triphenylphosphoranylidene)amino-derivatives.—Hitherto, the Kirsanov reaction [13] has always been used as the principal step for the conversion of (amino)-cyclophosphazenes into $N=PPh_3$ derivatives.[11,12,14] However, more routes for this conversion seem to be accessible, in particular the Appel reaction using the tetrachloromethane (CCl_4)–triphenylphosphine (PPh_3) system,[15,16] and the modified Mitsunobu reaction [17,18] using diethyl azodicarboxylate (dad) and PPh_3. We have tried to apply these two methods to convert $N_3P_3Cl_4(NH_2)_2$ (1) into $N_3P_3Cl_4(N=PPh_3)_2$ (3).

Reactions of compound (1) with dad and PPh_3 in diethyl ether (17 h, room temperature) afforded the product $N_3P_3Cl_4(NH_2)(N=PPh_3)$ (2) as the only cyclophosphazene derivative (Scheme 1). A yield of 43% was obtained using a molar ratio (1) : (dad) : (PPh_3) = 1 : 3.5 : 1.75. The desired bis($N=PPh_3$) derivative was never observed. The analogous reaction with a second bis(amino)cyclophosphazene, *viz.* geminal $N_3P_3(NMe_2)_4(NH_2)_2$, showed that the reaction is not of general use for the conversion of $P(NH_2)_2$ into $P(NH_2)$-

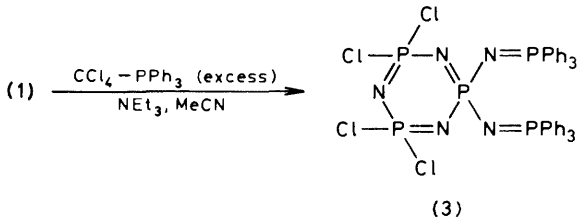


(1) (2)

Scheme 1.

($N=PPh_3$) groupings. The presence of electron-donating ligands (dimethylamino) apparently decreases the acidity of the NH_2 protons (which has been suggested to be an essential criterion for this reaction [18]) to such an extent that the reaction no longer proceeds.

By applying the Appel reaction we succeeded in preparing compound (3) from (1). Whereas reactions of compound (1) with a slight excess of PPh_3 [ratio (1) : (PPh_3) varying from 1 : 1.2 to 1 : 2.0] in the presence of excess of both tetrachloromethane and triethylamine in acetonitrile led predominantly to the formation of (2) (up to 35% yield), substantially contaminated with (3) and $N_3P_3Cl_5(N=PPh_3)$, reactions with a four- to five-fold excess of PPh_3 afforded 60% of (3) (Scheme 2). Obviously, under these circumstances



(3)

Scheme 2.

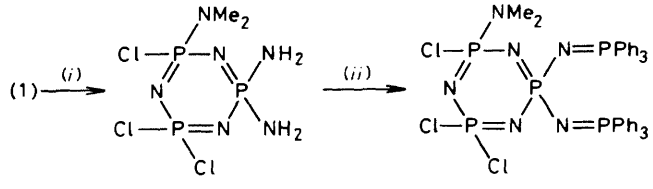
CCl_4–PPh_3 is a more reactive phosphorylating system than dad–PPh_3. The disadvantage of the possible chlorinating behaviour [Appel reaction mixtures contain PPh_3Cl_2 which is

known to convert (1) into $N_3P_3Cl_5(N{=}PPh_3)$[11] can apparently be minimized by using an excess of PPh_3. The high efficiency of the reagent is also reflected in its ability to convert $N_3P_3Cl_3(NMe_2)(NH_2)_2$ (4) into $N_3P_3Cl_3(NMe_2)(N{=}PPh_3)_2$ (5), and $N_3P_3(NMe_2)_4(NH_2)_2$ into $N_3P_3(NMe_2)_4(N{=}PPh_3)_2$ (7).

Reactions of Compound (3) *with Dimethylamine.*—Investigations of the behaviour of compound (3) in nucleophilic substitution reactions with dimethylamine were hampered by a number of factors. First, (3) was only well soluble in a limited number of solvents (aromatic and chlorinated hydrocarbons, tetrahydrofuran), and it generally showed such a low reactivity in these solvents that an excess of amine had to be used for the preparation of partly aminated derivatives. Usually, this resulted in the formation of crude products, that consisted of a mixture of compounds. In these mixtures the presence of (3), the monosubstituted derivative $N_3P_3Cl_3(NMe_2)(N{=}PPh_3)_2$ (5), one disubstituted derivative $N_3P_3Cl_2(NMe_2)_2(N{=}PPh_3)_2$ (6), and the tetrasubstituted derivative $N_3P_3(NMe_2)_4(N{=}PPh_3)_2$ (7) could be established. The isolation of pure compounds was further hampered by the ease with which the derivatives formed adducts, *e.g.* with the liberated HCl [(6) and (7)], with the solvent (in particular acetonitrile), and with each other [*e.g.* formation of (3)·(5)]. Therefore, yields of pure products were low.

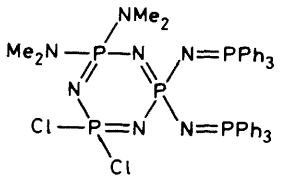
Secondly, a reliable interpretation of the ^{31}P n.m.r. spectra of the crude products (generally an excellent technique for determining their composition) appeared to be impossible. The signals were always broad, probably due to proton-exchange processes between the products and simultaneously formed HCl adducts. A reasonable insight into the composition of the reaction mixtures could be obtained by saturating their solution in $CHCl_3$ with gaseous HCl, thus converting (6) and (7) into HCl adducts, and then recording the ^{31}P n.m.r. spectra. However, it cannot be completely excluded that in this way minor constituents of the mixtures have escaped detection.

The monosubstituted derivative $N_3P_3Cl_3(NMe_2)(N{=}PPh_3)_2$ (5) was the main product of a reaction of (3) with dimethylamine (molar ratio 1 : 2) in chloroform. It could, however, never be freed from contaminations, although an analytically pure 1 : 1 adduct with the starting material (3) (m.p. 180—182 °C) was isolated. A far more profitable route to pure (5) was by the dimethylaminolysis of (1) to the mono(dimethylamino) derivative (4) and subsequent Appel reaction (Scheme 3).



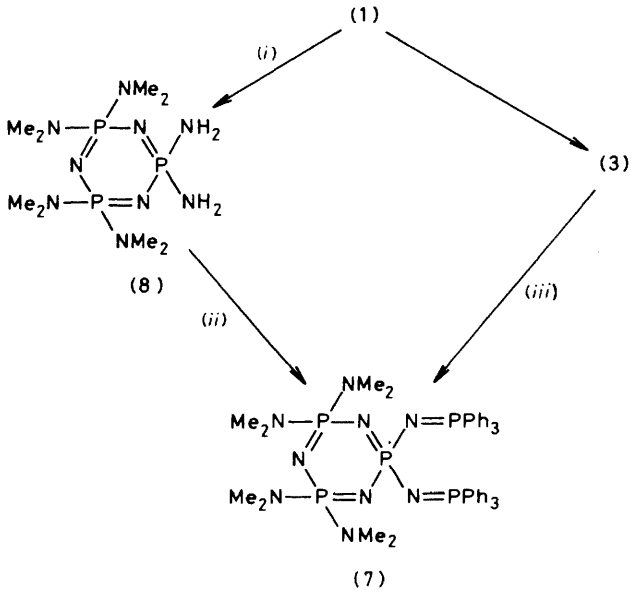
Scheme 3. (*i*) NMe_2H (1 : 2), Et_2O; (*ii*) CCl_4–PPh_3, NEt_3, MeCN

Reaction of compound (3) with dimethylamine in a 1 : 15 molar ratio in boiling benzene afforded mainly a bis(dimethylamino) derivative in addition to minor quantities of the tetrasubstituted one. Its ^{31}P and ^1H n.m.r. spectra [*e.g.* $^3J(PH)$ = 11.3 Hz] unambiguously showed it to possess the geminal structure $\overline{NPCl_2NP(NMe_2)_2NP(N{=}PPh_3)_2}$ (6); isolation of pure (6) could be performed in only 10% yield. Reactions with a stoicheiometric quantity of amine in acetonitrile or chloroform also afforded (6), but the product mixtures were more



complex. Neither non-geminal bis- nor tris-(dimethylamino) derivatives were ever observed.

The tetrakis(dimethylamino) derivative $N_3P_3(NMe_2)_4(N{=}PPh_3)_2$ (7) was readily prepared in acetonitrile [in which (3) is only sparingly soluble] by reaction of (3) with an excess of amine. It was also prepared from (1) by reaction with an excess of dimethylamine in diethyl ether, affording $N_3P_3(NMe_2)_4(NH_2)_2$ (8), followed by the Appel reaction. Along



Scheme 4. (*i*) NMe_2H (excess), Et_2O; (*ii*) CCl_4–PPh_3, NEt_3, MeCN; (*iii*) NMe_2H (excess), MeCN

the former route (7) was isolated as its HCl adduct, along the latter as its 2HCl adduct.

To our knowledge, a predominantly geminal dimethylaminolysis pattern for cyclophosphazenes has never been reported before, although indications exist that $N_3P_3Cl_4Ph(N{=}PPh_3)$ behaves similarly to (3).[19] A geminal pattern is expected to be connected with the occurrence of a first-order type reaction mechanism. Recently, it has been shown that cyclophosphazenes are able to undergo S_N1-type substitutions, when the S_N2-type substitution rate is decreased by the presence of a sufficient number of electron-donating groups {*e.g.* in $N_3P_3Cl(OPh)_5$ and $[NPCl(NMe_2)]_3$}.[10] It now appears

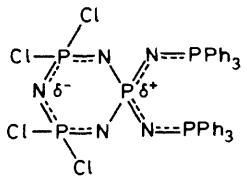
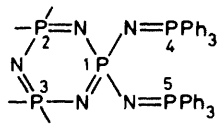


Table 1. ^{31}P N.m.r. data



Compound	Chemical shift, δ/p.p.m.					Coupling constant, ^2J/Hz				
	P^1	P^2	P^3	P^4	P^5	P^1P^2	P^1P^3	P^2P^3	P^1P^4	P^1P^5
(1) $N_3P_3Cl_4(NH_2)_2$	8.4	21.1				50.4				
(4) $N_3P_3Cl_3(NMe_2)(NH_2)_2$	11.3	22.8 [a]	27.4			46.4	46.4	53.7		
(8) $N_3P_3(NMe_2)_4(NH_2)_2$	17.8	26.4				41.8				
(2) $N_3P_3Cl_4(NH_2)(N{=}PPh_3)$	−1.6	16.9		12.1		43.5			27.0	
(3) $N_3P_3Cl_4(N{=}PPh_3)_2$	−10.9	13.4			5.9	35.8			20.6	
(5) $N_3P_3Cl_3(NMe_2)(N{=}PPh_3)_2$ [b]	−8.0	15.5 [a]	24.4	4.28	4.34	37.6	36.3	59.5	22.5	19.3
(6) $N_3P_3Cl_2(NMe_2)_2(N{=}PPh_3)_2$	−4.7	18.9 [a]	20.5		1.8	43.4	39.7	47.7	16.6	
(6)·HCl	−11.0	15.4 [a]	21.5		8.8	21.1	18.2	40.4	13.8	
(7) $N_3P_3(NMe_2)_4(N{=}PPh_3)_2$	1.9	25.0			2.6	40.1			10.3	
(7)·HCl	−6.0	19.6	21.9		5.9	29.5	26.1	38.9	11.6	
(7)·2HCl [b]	−14.2	18.9			10.2	*c*			16.6	

[a] δ(PCl_2). [b] MeCN adducts gave identical values. [c] Insufficient resolution (see text).

Table 2. Analytical data of purified compounds

Compound	M.p.[a]/°C	Analysis [b]/%			
		C	H	N	Cl
(2)	178—178.5	38.15 (38.00)	3.05 (3.00)	12.45 (12.30)	24.80 (24.90)
(3)	195.5—197.5	52.20 (52.15)	3.80 (3.65)	8.90 (8.45)	17.15 (17.10)
(5)·MeCN	174—176.5	54.50 (54.65)	4.50 (4.45)	10.85 (11.15)	12.35 (12.10)
(6)	205.5—208	56.25 (56.75)	5.00 (5.00)	11.60 (11.60)	8.60 (8.35)
(7) [c]	206—207	61.00 (61.20)	6.25 (6.30)	14.70 (14.60)	—
(7)·2HCl	219—220	56.30 (56.40)	6.10 (6.00)	13.35 (13.45)	7.60 (7.55)
(7)·2HCl·MeCN	216—220	56.20 (56.50)	6.10 (6.10)	14.35 (14.30)	7.35 (7.25)

[a] Uncorrected. [b] Calculated values in parentheses. [c] P 18.10 (17.90%).

that the presence of two strongly electron-donating $N{=}PPh_3$ ligands causes such a charge separation within the molecule that a S_N1-type reaction mechanism, initiated by chloride elimination, is preferred over a S_N2 type. The relatively long P–Cl distances (up to 2.04 Å) in crystalline (3) [4] also support a S_N1-type mechanism.

^{31}P *N.M.R. Spectra.*—^{31}P n.m.r. parameters are listed in Table 1. The spectra showed the resonance patterns predicted by first-order rules. Four-bond P–P couplings were not observed. In compound (5) P^4 and P^5 are inequivalent due to their different positions (*cis*/*trans*) with respect to the amino-ligand; in (7)·HCl, P^2 and P^3 are inequivalent due to the attachment of the proton to a nitrogen atom adjacent to the $P(N{=}PPh_3)_2$ centre.

In order to look for meaningful trends in the different parameters, some series of compounds have been compared. (*a*) In the series (1)—(3), (4) and (5), and (8) and (7), the ligands at P^2 and P^3 are identical and those at P^1 change from $(NH_2)_2$ *via* $(NH_2)(N{=}PPh_3)$ to $(N{=}PPh_3)_2$. The chemical shifts of P^2 and P^3 reflect the increasing input of electrons into the ring with increasing number of $N{=}PPh_3$ ligands; the gradual shielding is more distinct for PCl_2 groupings. The large shielding of the P^1 signal upon the conversion of NH_2 into $N{=}PPh_3$ has been suggested to be largely due to the change of hybridization at the exocyclic nitrogen atom.[20] (*b*) In the series (3), (5), (6), and (7) with identical ligands at P^1, the number of dimethylamino-ligands at P^2 and P^3 gradually increases. The chemical shift of P^2 [PCl_2 or $P(NMe_2)_2$] increases with increasing number of amino-ligands at P^3, which is a general trend for cyclophosphazenes;[21] P^1 also shows a gradual downfield shift. The shifts of P^4 and P^5 show a slight upfield trend upon progressive substitution, which is due to the increasing competitive electron donation of the amino-ligands. (*c*) In the series (7), (7)·HCl, and (7)·2HCl, P^4 and P^5 are gradually deshielded, which might reflect the increasing electron-acceptor ability of the ring with increasing degree of protonation (both the first and second protonation occur at ring nitrogen atoms, see next section). The induced positive charge is thus delocalized towards the exocyclic N=P fragments. The large shielding of P^1 upon protonation reflects the important change in the bonding around this atom during the protonation process.

It is possible to express ^2J(PP) within cyclophosphazenes in terms of ligand parameters,[22] but Table 1 shows that such a simple relationship is not valid for the compounds under investigation.

Adducts (7)·HCl *and* (7)·2HCl.—The presence of two strongly electron-donating ligands renders the compounds under investigation susceptible to protonation. The bis-(dimethylamino) derivative (6) can readily be converted into (6)·HCl, and the combined electron-donor ability of two (triphenylphosphoranylidene)amino- and four dimethylamino-ligands makes (7) an even stronger base than simple organic amines; this explains the formation of (7)·HCl in substitution reactions even in the presence of an excess of amine. Furthermore, (7) and (7)·HCl can be readily converted into (7)·2HCl, although the isolation of the latter after the Appel reaction with (8) is probably a consequence of the work-up procedure

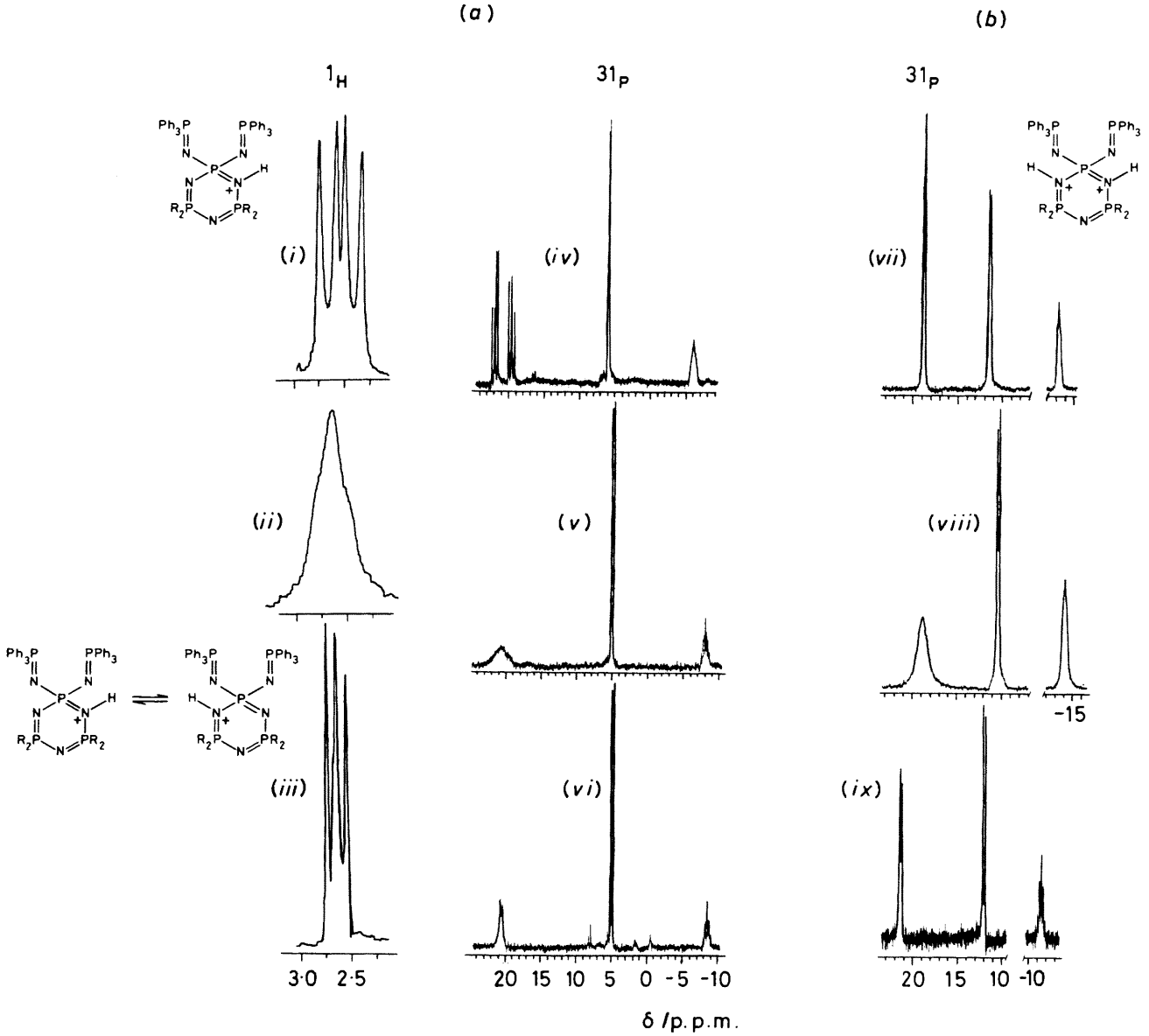
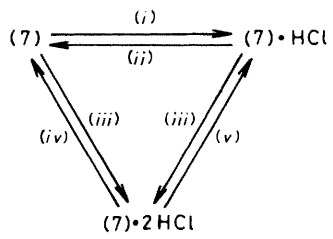


Figure. Temperature-dependent n.m.r. spectra of (7)·HCl (*a*) and (7)·2HCl (*b*), R = NMe_2. Conditions: (*i*) 20, (*ii*) 115, (*iii*) 175 °C in $C_6D_5NO_2$; (*iv*) 18, (*v*) 130, (*vi*) 150 °C in $(CD_3)_2SO$; (*vii*) −30, (*viii*) 21 °C in $CDCl_3$, (*ix*) 70 °C in CD_3CN

employed. The free base (7) and its (water-soluble) salts (7)·HCl and (7)·2HCl can be interconverted by simple experiments (Scheme 5).

According to earlier basicity studies [8] the most basic nitrogen atoms in compound (7) are those adjacent to the $P(N{=}PPh_3)_2$ centre, and this is in line with the inequivalence of



Scheme 5. (*i*) NEt_3·HCl, $CHCl_3$; (*ii*) KOH, $CHCl_3$–H_2O; (*iii*) HCl, $CHCl_3$; (*iv*) KOH, H_2O; (*v*) NEt_3, $CHCl_3$

P^2 and P^3 observed in the ^{31}P and ^1H n.m.r. spectra of (7)·HCl (ambient temperature). At high temperatures (>140 °C) P^2 and P^3 become equivalent due to a rapid proton exchange between the two equivalent nitrogen atoms, as depicted in the Figure. The exchange process is probably intermolecular, analogous to the mechanism proposed for the proton exchange in $[N_3P_3Me_6H]^+$.[23]

For (7)·2HCl a related exchange process could be observed. At −30 °C as well as +70 °C (in MeCN) the spectrum showed the splitting pattern of a A_2MX_2 spin system, with equivalent P^2 and P^3, whereas in the range −15 to +40 °C the doublet due to the $P(NMe_2)_2$ groupings was broadened (maximum broadening at about +20 °C, see Figure). It is difficult to give an exact explanation for these observations. At low temperatures the structural assignment is unambiguous; as the first proton is attached to an endocyclic nitrogen atom adjacent to the $P(N{=}PPh_3)_2$ centre [*cf.* the situation in (7)·HCl], the second proton must be attached to the other endocyclic nitrogen atom adjacent to the $P(N{=}PPh_3)_2$ centre in order to

arrive at an equivalence of P^2 and P^3 (Figure). At +70 °C a rapid intermolecular proton exchange is assumed to take place, by which the overall symmetry of the system is not affected. It should be emphasized again that the two ring nitrogen atoms α to the $P(N{=}PPh_3)_2$ grouping are much better proton acceptors than the other ones; this might suggest that at high temperatures a situation exists in which protons rapidly exchange between these two nitrogen atoms. However, the data do not permit a reliable description of the exchange mechanism.

Experimental

General.—All experiments were carried out under dry nitrogen. Triethylamine was purified by distillation over KOH pellets. Solutions of dimethylamine (*ca.* 1 mol dm^{-3}) were prepared by distillation of the amine through a KOH column into a vessel containing the required solvent. The concentrations were determined prior to use by means of titration. Triphenylphosphine was used as purchased (Merck). Solvents were purified and dried by conventional methods. The compound $N_3P_3Cl_4(NH_2)_2$ (1) was prepared as described elsewhere.[24]

Proton n.m.r. spectra were recorded with a JEOL C60-HL instrument, using $SiMe_4$ as internal reference; ^{31}P n.m.r. spectra (proton-noise decoupled) were taken with a Nicolet NT 200 spectrometer, operating at 81.0 MHz; $(NPCl_2)_3$ was used as external reference (19.9 p.p.m.). Spectra were taken of solutions in $CDCl_3$ unless otherwise stated; the ^2H resonance line of the solvent was used for field–frequency lock (^{31}P). Chemical shifts are positive to low field.

Preparation of (Triphenylphosphoranylidene)amino-derivatives.—(*i*) $N_3P_3Cl_4(NH_2)(N{=}PPh_3)$ (2). A solution of diethyl azodicarboxylate (8.6 mmol) in diethyl ether (35 cm^3) was cooled at −17 °C. Triphenylphosphine (4.3 mmol) and compound (1) (2.4 mmol) were added and the reaction mixture was allowed to warm slowly to room temperature and then stirred for 17 h at this temperature. The white precipitate was filtered off, washed with hot water, and recrystallized from diethyl ether. Yield 43% of pure (2), m.p. 177.5—178.5 (lit.,[11] 173—174 °C).

(*ii*) $N_3P_3Cl_4(N{=}PPh_3)_2$ (3). To a solution of compound (1) (6.5 mmol) and triphenylphosphine (29.8 mmol) in acetonitrile (40 cm^3) were added an excess of triethylamine and tetrachloromethane (45 mmol). To start the reaction the mixture was warmed at 40 °C for 30 min and then stirred for 17 h at room temperature. After evaporation of the solvent under reduced pressure, the brown residue was washed with ice-cold acetonitrile then water and recrystallized from acetonitrile. Yield 60% of pure (3), m.p. 195.5—197.5 (lit.,[11] 199—201 °C).

(*iii*) $N_3P_3Cl_3(NMe_2)(N{=}PPh_3)_2$ (5). A 1 mol dm^{-3} solution of dimethylamine (4.0 cm^3) in diethyl ether was added dropwise to a stirred solution of compound (1) (2.0 mmol) in diethyl ether (20 cm^3), cooled at −30 °C. After completion of the addition the mixture was allowed to warm slowly to room temperature and then stirred for 17 h at this temperature. After removal of dimethylamine hydrochloride the solvent was evaporated under reduced pressure. The white solid thus obtained contained almost exclusively (4) [^1H n.m.r. (NMe_2 region): δ 2.56, $^3J(PH)$ 16.5 Hz] and was used in the following reaction without further purification.

The white solid and triphenylphosphine (15.2 mmol) were dissolved in acetonitrile (20 cm^3). An excess of triethylamine and tetrachloromethane (24 mmol) were added and the mixture was stirred at room temperature for 65 h. After evaporation of the solvent under reduced pressure the residue was extracted twice with benzene. The combined extracts were evaporated to dryness and the crude product was recrystallized from diethyl ether–acetonitrile (1 : 1). Overall yield 35% of (5)·MeCN [^1H n.m.r. (NMe_2 region): δ 2.31 $^3J(PH)$ 15.8 Hz].

(*iv*) $N_3P_3(NMe_2)_4(NH_2)_2$ (8). A solution of compound (1) (10 mmol) in diethyl ether (30 cm^3) was added dropwise to a stirred solution of an excess of dimethylamine in diethyl ether (150 cm^3), cooled at −30 °C. The mixture was allowed to warm slowly to room temperature and was then stirred for 17 h at this temperature. After removal of dimethylamine hydrochloride the solvent was evaporated under reduced pressure and the crude product was recrystallized from n-hexane. Yield 89% of pure (8) [^1H n.m.r. (NMe_2 region): δ 2.62, $^3J(PH)$ 15.8 Hz], m.p. 140.5—142.5 (lit.,[25] 155 °C).

(*v*) $N_3P_3(NMe_2)_4(N{=}PPh_3)_2$ (7). To a solution of compound (8) (4.1 mmol) and triphenylphosphine (30.7 mmol) in acetonitrile (60 cm^3) an excess of triethylamine and tetrachloromethane (46 mmol) were added. The mixture was stirred for 17 h at room temperature. After evaporation of the solvent under reduced pressure the residue was extracted twice with benzene. The combined extracts were evaporated to dryness, and the crude product was recrystallized from diethyl ether–acetonitrile (1 : 1). Yield 60% of (7)·2HCl·MeCN [^1H n.m.r. (NMe_2 region): δ 2.66, $^3J(PH)$ 11.3 Hz]. The hydrochloride could be quantitatively converted into the free base (7) by treatment with a two-fold excess of KOH in water. Recrystallization of the white precipitate from acetonitrile afforded pure (7) [^1H n.m.r. (NMe_2 region): δ 2.45, $^3J(PH)$ 11.3 Hz].

Substitution Reactions of Compound (3) *with Dimethylamine.*—(*a*) $N_3P_3Cl_2(NMe_2)_2(N{=}PPh_3)_2$ (6). A 1 mol dm^{-3} solution of dimethylamine (15 cm^3) in benzene was added to a solution of compound (3) (1 mmol) in benzene (20 cm^3) and the mixture was refluxed for 17 h. After removal of dimethylamine hydrochloride the solvent was evaporated under reduced pressure and the crude product recrystallized from acetonitrile. Yield 10% of pure (6) [^1H n.m.r. (NMe_2 region): δ 2.36, $^3J(PH)$ 11.3 Hz].

(*b*) $N_3P_3(NMe_2)_4(N{=}PPh_3)_2$ (7). A 1 mol dm^{-3} solution of dimethylamine (40.0 cm^3) in acetonitrile was added dropwise to a stirred suspension of compound (3) (1.7 mmol) in acetonitrile (20 cm^3). After completion of the addition all (3) had dissolved and the mixture was stirred for 17 h at room temperature. After evaporation of the solvent under reduced pressure the residue was extracted twice with benzene and the combined extracts were evaporated to dryness. The remaining white solid could not be purified by recrystallization. N.m.r. spectroscopy indicated that the product was the monohydrochloride salt of (7) [^1H n.m.r. (NMe_2 region): δ 2.54, $^3J(PH)$ 11.3; 2.42, $^3J(PH)$ 11.3 Hz] (yield 96%).

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