Reactivity of Hexachlorocyclotriphosphazene towards Alkyl-lithium Reagents

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Reactions of $(NPCl_2)_3$ with LiMe or LiBu^t and an excess of propan-2-ol at −60 °C in tetrahydrofuran lead to complex reaction mixtures containing cyclic derivatives in 80—90% yield. The composition of each reaction mixture has been analyzed by ^{1}H and ^{31}P n.m.r. spectrometry. The n.m.r. data thus obtained indicate the presence of a novel cyclophosphazene, *viz.* $NP(H)OPr^i(NPCl_2)_2$ and several alkyl-substituted cyclophosphazenes. Typical compounds were isolated and characterized as their 2,2,2-trifluoroethoxy-substituted derivatives. The structural characterizations of the reaction products are described together with the appropriate reaction pathways, based on an initial metal–halogen exchange process.

The reactivity of hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (**1**), towards organometallic compounds has gained considerable interest.

Around 1970 Biddlestone and Shaw [1,2] reported the reactions of (**1**) with MgPhBr in several solvent mixtures and with $MgPh_2$ in dioxane.[1,2] The products formed in the latter reaction pointed to complicated reaction mechanisms.

Ten years later Allcock *et al.*[3–5] investigated the reactions of (**1**) with $[\{CuI(PBu_3)\}_4]$-MgRCl (R = alkyl) and MgRCl (R = Ph or alkyl) in tetrahydrofuran. A wide range of alkylated cyclophosphazenes and bi(cyclophosphazenes) could be prepared.

Reactions of (**1**) with LiR (R = alkyl or aryl) have been reported to give resinous material as a result of extensive ring degradation.[6,7] However, Allcock *et al.*[8] reported the formation of metallocene substituted derivatives of (**1**) using lithium metallocene complexes.

Recently we published preliminary results concerning the reactions of (**1**), $(NPCl_2)_4$, and *trans*-$NPCl_2(NSOPh)_2$ with LiR (R = Me or Bu^t), which clearly indicate that under carefully chosen conditions ring degradation can be avoided.[9,10]

Here we report a complete picture of the reactivity of (**1**) towards LiMe and LiBu^t, together with a discussion of the reaction mechanism.

Results and Discussion

An extensive search into the proper reaction conditions to obtain high yields of organo-substituted cyclophosphazenes using alkyl-lithium reagents resulted in the following procedure. Reactions of (**1**) with LiR, molar ratio 1:1, 1:2 (R = Me or Bu^t) and 1:3 (R = Bu^t), are carried out in tetrahydrofuran (thf) while keeping the temperature below −60 °C. The reaction mixtures are treated with a five-fold excess of propan-2-ol at −60 °C and allowed to warm to room temperature. Evaporation of the solvent and subsequent extraction of the remainder with pentane gives a mixture of products. The high yield (80—90% by weight) thus obtained allows a detailed investigation of the mechanism involved.

In order to obtain information about all the reaction products the crude reaction mixtures were analyzed by ^{31}P and ^{1}H n.m.r. spectrometry. Absolute yields (mol%) as well as total yields of cyclic material are collected in Table 1 (see also Experimental section).

Table 1. Absolute yields (mol%) of compounds from the reactions of (**1**) (500 mg) with LiR (R = Me or Bu^t) and propan-2-ol. Total yields (mg) are given in parentheses

		Molar ratio (**1**):LiR				
		R = Me		R = Bu^t		
		1:1	1:2	1:1	1:2	1:3
(**1**)	$(NPCl_2)_3$	10		60	10	
(**2**)	$NP(H)OPr^i(NPCl_2)_2$	60	30	20	50	30
(**6**), (**7**)			20			
(**3**), (**11**)	$NP(H)R(NPCl_2)_2$*	10	10	10	25	55
(**4**)	$(N_3P_3Cl_4Me)_2$		15			
(**12**)	$NP(Cl)Bu^t(NPCl_2)_2$				5	5
(**5**)	$NPMe_2(NPCl_2)_2$		5			
	Total	80 (405)	80 (370)	90 (450)	90 (430)	90 (450)

* R = Me (**3**) or Bu^t (**11**).

A. Equimolar Reaction of (**1**) *with* LiMe; *Subsequent Treatment with Propan-2-ol.*—The n.m.r. spectra of the reaction mixture (Figure 1, Table 2) indicate the presence of a novel cyclophosphazene (**2**), besides (**1**) and a small amount of $NP(H)Me(NPCl_2)_2$ (**3**) [for structure assignment of (**3**) see *B*].

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**2**) consists of a simple AB_2 spin system, with resonance lines at 2.5 [triplet, ^2J(PP) 26.0 Hz] and 20.9 p.p.m. [doublet, ^2J(PP) 26.0 Hz, PCl_2 region]. In the proton-coupled spectrum the doublet becomes a triplet [^2J(PP) 26.0, ^3J(PH) 11.9 Hz]; the triplet at 2.5 p.p.m. splits into two multiplets [^3J(PH) 11.6 Hz] with large coupling constant [^1J(PH) 719 Hz], which is characteristic for a P–H bond and resembles that of the well known dialkyl phosphites $P(O)H(OR)_2$.[11] Moreover the ^2J(PP) value of 26.0 Hz is significantly larger than usually found for alkyl-substituted cyclophosphazenes.

The ^{1}H n.m.r. spectrum shows the characteristics of an isopropoxy grouping [doublet (Me) at 1.3 p.p.m., ^3J(HH) 5.8 Hz; multiplet (CH) at 4.5 p.p.m.] and two groups (triplets) of hydrido resonances at 0.9 and 12.9 p.p.m. [^1J(PH) 719, ^3J(PH) 11.9 Hz]. According to these data the structure $NP(H)OPr^i(NPCl_2)_2$ is assigned to (**2**).

B. Reaction of (**1**) *with Two Equivalents of* LiMe; *Subsequent Treatment with Propan-2-ol.*—Analysis of the crude reaction mixture by ^{31}P n.m.r. (Figure 2, Table 2) pointed to the presence of six compounds, four of them being hydridocyclophosphazenes, including (**2**) [based on ^1J(PH) values in the range 500—700 Hz]. Comparison of the n.m.r. parameters with data on alkylcyclophosphazenes[3–5] allowed the assign-

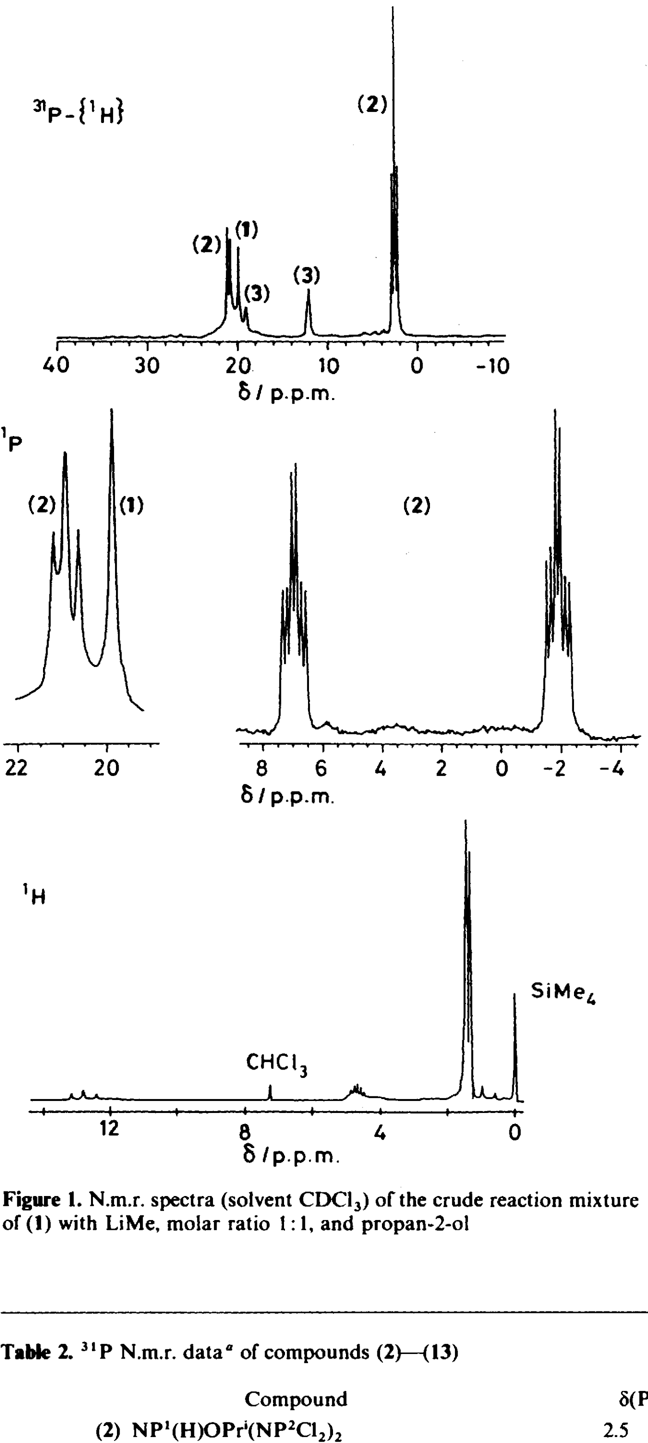


Figure 1. N.m.r. spectra (solvent $CDCl_3$) of the crude reaction mixture of (**1**) with LiMe, molar ratio 1 : 1, and propan-2-ol

ment of $NP(H)Me(NPCl_2)_2$ (**3**), the bi(cyclophosphazene) $(N_3P_3Cl_4Me)_2$ (**4**), and $NPMe_2(NPCl_2)_2$ (**5**) (Table 2). Because of the complexity of the spectra the presence of (**3**) and (**4**) was confirmed by synthesizing authentic samples[3,5] (Table 2).

With respect to the two remaining compounds the $^{31}P-\{^1H\}$ n.m.r. spectrum [Figure 2] shows two doublets [$^2J(PP)$ 26.4 and 18.6 Hz, respectively] in the $P(H)OPr^i$ region; the proton coupled spectrum [Figure 2] shows $^1J(PH)$ values of 668 and 699 Hz. However, additional groups of resonance lines with compatible $^2J(PP)$ values could not be detected. We presume that besides the compounds (**2**)—(**5**) two other cyclic derivatives (**6**) and (**7**) were formed, which both incorporate a $P(H)OPr^i$ moiety (see *D*).

Although most compounds could be identified by ^{31}P n.m.r. spectrometry the elucidation of the reaction mechanism needed full characterization of the main products. However, the moisture sensitivity and instability of the hydridocyclophosphazenes prevented separation by means of h.p.l.c. As in general the instability of such compounds is related to the presence of PCl_2 groupings this difficulty was circumvented by substituting all the chlorine atoms by 2,2,2-trifluoroethoxy groups.

In a typical experiment the reaction mixture of (**1**) and LiMe, molar ratio 1 : 2, and propan-2-ol was treated with sodium 2,2,2-trifluoroethoxide and an excess of 2,2,2-trifluoroethanol (in order to avoid breaking of the P–H bond) in thf at 0 °C. According to ^{31}P n.m.r. spectrometry (Table 2) the crude reaction mixture contained three cyclic derivatives (**8**), (**9**), and (**10**), two of them being hydridocyclophosphazenes (Table 2). Residual resonance lines represented less than 5% of the total amount of cyclic derivatives.

Separation by means of h.p.l.c. gave $NP(H)OPr^i[NP(OCH_2CF_3)_2]_2$ (**8**) and $NP(Me)OCH_2CF_3[NP(OCH_2CF_3)_2]_2$ (**9**), which could be fully characterized. Compound (**9**) is known to be a product of the reaction of (**4**) with sodium 2,2,2-trifluoroethoxide.[12] Compound (**10**) appeared to decompose during the h.p.l.c. experiment.

From the ^{31}P n.m.r. data of the reaction mixture the structure $NP(H)Me[NP(OCH_2CF_3)_2]_2$ was assigned to (**10**), which was confirmed by comparison with the ^{31}P n.m.r. data of an authentic sample[12] (Table 2).

C. Reactions of (**1**) *with* $LiBu^t$, *Molar ratio* 1 : 1, 1 : 2, *or* 1 : 3; *Subsequent Treatment with Propan-2-ol.*—The $^{31}P-\{^1H\}$ n.m.r. spectrum of the reaction mixture of (**1**) with $LiBu^t$, molar ratio 1 : 1, and propan-2-ol [Figure 3(*a*)] shows, besides a considerable amount of the starting material (**1**), the presence of two cyclic derivatives, *i.e.* (**2**) and $NP(H)Bu^t(NPCl_2)_2$ (**11**). Using

Table 2. ^{31}P N.m.r. data[a] of compounds (**2**)—(**13**)

Compound	δ(P¹)	δ(P²)	$^2J(PP)$	$^1J(PH)$
(**2**) $NP^1(H)OPr^i(NP^2Cl_2)_2$	2.5	20.9	26.0	719
(**3**) $NP^1(H)Me(NP^2Cl_2)_2$	12.1 (12.1)	19.1 (19.1)	*b*	568 (568)
(**4**) $[NP^1Me(NP^2Cl_2)_2]_2$	26.3 (26.3)	19.6 (19.6)	*b*	
(**5**) $NP^1Me_2(NP^2Cl_2)_2$	35.7; 35.7[c]	*d*; 18.0[c]	*b*; 8.9[c]	
(**7**)	4.8	*d*	*d*	668
(**6**)	5.7	*d*	*d*	699
(**8**) $NP^1(H)OPr^i[NP^2(OCH_2CF_3)_2]_2$	11.6	15.4	48.1	637
(**9**) $NP^1(Me)OCH_2CF_3[NP^2(OCH_2CF_3)_2]_2$	39.6; 39.8[c]	15.6; 15.6[c]	47.9; 47.9[c]	
(**10**) $NP^1(H)Me[NP^2(OCH_2CF_3)_2]_2$	17.2 (17.2)	14.8 (14.8)	30.4 (30.4)	542 (542)
(**11**) $NP^1(H)Bu^t(NP^2Cl_2)_2$	32.6; 32.3[c,e]	19.3; 18.4[c,e]	*b*	543; 543[c,e]
(**12**) $NP^1(Cl)Bu^t(NP^2Cl_2)_2$	57.2	21.9	*b*	
(**13**) $NP^1(H)Bu^t[NP^2(OCH_2CF_3)_2]_2$	37.4	15.8	21.6	527

[a] Chemical shifts in p.p.m.; coupling constants in Hz; solvent $CDCl_3$; values of authentic samples in parentheses. [b] Unresolved lines. [c] Literature values: (**5**), ref. 4; (**9**), ref. 12; (**11**), ref. 3. [d] Hidden lines. [e] Observed in tetrahydrofuran.

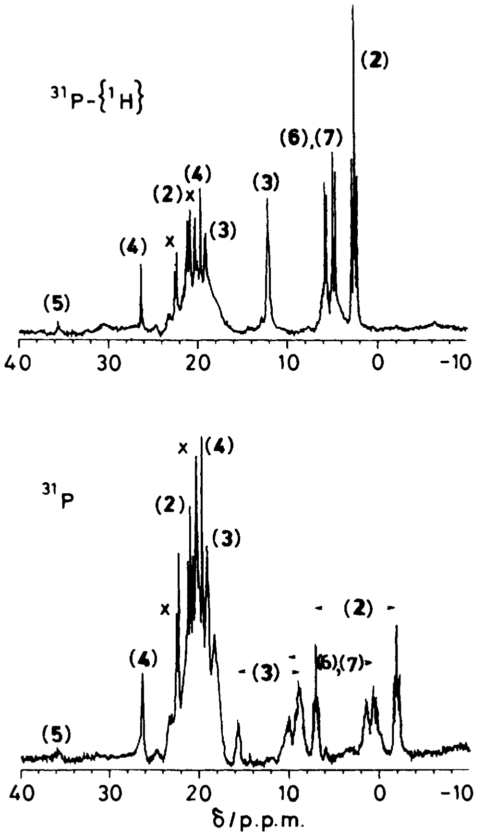


Figure 2. ^{31}P N.m.r. spectra (solvent $CDCl_3$) of the crude reaction mixture of (**1**) with LiMe, molar ratio 1:2, and propan-2-ol (x = unidentified lines)

two equivalents of $LiBu^t$ [Figure 3(*b*)] compound $NP(Cl)Bu^t(NPCl_2)_2$ (**12**) can be detected. Both (**11**) and (**12**) have been described previously.[3,5]

As even in the 1:1 reaction an appreciable amount of the starting material (**1**) remained unreacted the experiment was also carried out with three equivalents of $LiBu^t$ (Table 2).

In a typical experiment the reaction mixture of (**1**) with $LiBu^t$, molar ratio 1:3, and propan-2-ol was treated with sodium 2,2,2-trifluoroethoxide as described under *B*. H.p.l.c. experiments gave two compounds, $NP(H)OPr^i[NP(OCH_2CF_3)_2]_2$ (**8**) and $NP(H)Bu^t[NP(OCH_2CF_3)_2]_2$ (**13**), which were fully characterized.

D. Reaction Routes and Mechanism.—As proposed for the formation of the hydridocyclophosphazenes (**3**) and (**11**) and the bi(cyclophosphazene) (**4**) in the reaction of (**1**) with Grignard reagents[3,5] we also assume that under our experimental conditions a metal–halogen exchange process is operative.

The appearance of (**2**), which is the predominant product in reactions of (**1**) with LiMe or $LiBu^t$ (molar ratio 1:1) and propan-2-ol, also points to the initial formation of a lithiocyclophosphazene, $NLiPCl(NPCl_2)_2$ (Scheme 1). Although no detailed information is available, a possible mechanism involves the protonation of the lithiated complex by propan-2-ol to give $NP(H)Cl(NPCl_2)_2$. The most plausible continuation of the reaction is a simple nucleophilic substitution by lithium isopropoxide at the P(H)Cl centre of $NP(H)Cl(NPCl_2)_2$, assuming that a P(H)Cl moiety is far more reactive towards a nucleophile than a PCl_2 moiety.

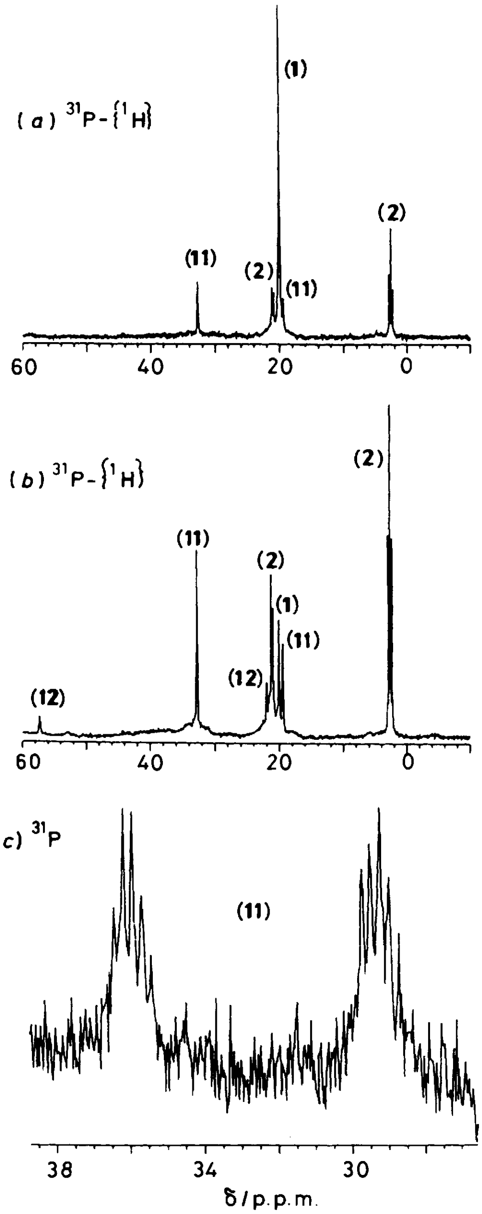
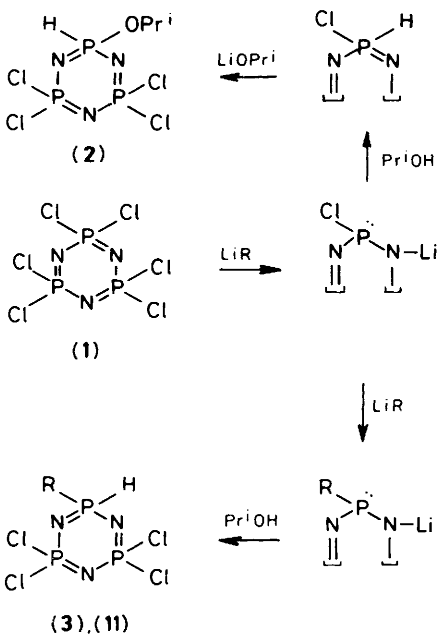


Figure 3. ^{31}P N.m.r. spectra (solvent $CDCl_3$) of the crude reaction mixtures of (**1**) with $LiBu^t$, molar ratio 1:1 (*a*) or 1:2 (*b*), (*c*), and propan-2-ol

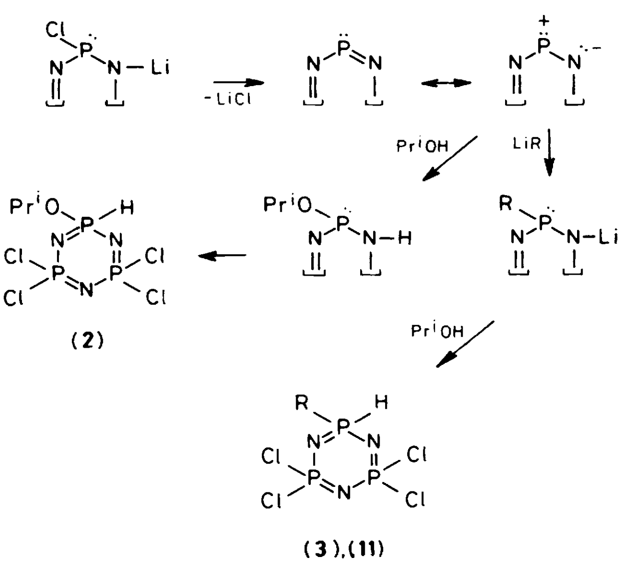
Nucleophilic substitution by LiR (R = Me or Bu^t) at the $\ddot{P}Cl$ centre of $NLiPCl(NPCl_2)_2$ leads to $NLiPR(NPCl_2)_2$, whereas subsequent protonation by propan-2-ol gives (**3**) and (**11**).

A totally different approach to explain the formation of compounds (**2**), (**3**), and (**11**) is visualized in Scheme 2. The first step is essentially the same as depicted in Scheme 1, *i.e.* formation of $NLiPCl(NPCl_2)_2$ according to a metal–halogen exchange process. This step can be followed by elimination of lithium chloride leading to a cyclophosphazene with a phosphorus(III) atom, whereas subsequent addition of propan-2-ol gives (**2**).

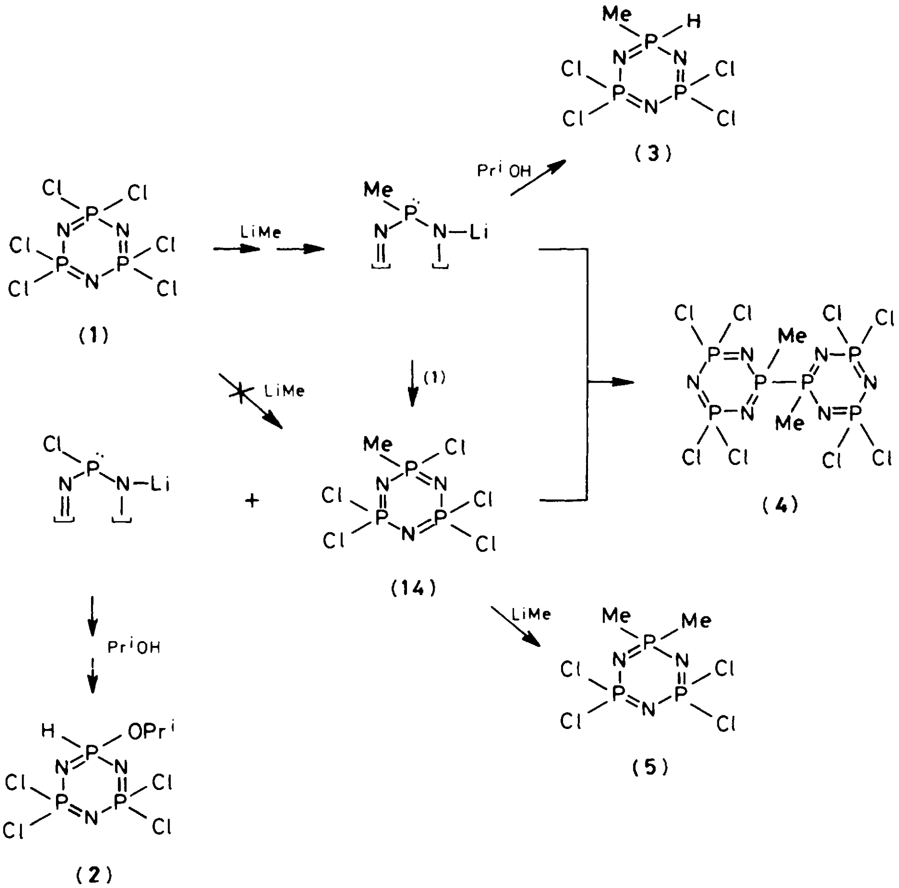
The appearance of $NP(NPCl_2)_2$, incorporating a phosph(III)azene moiety can be compared with several phosph(III)azenes, *e.g.* R^1–P=N–R^2 [R^1 = $N(SiMe_3)_2$, R^2 = $SiMe_3$; R^1 = R^2 = Bu^t].[13,14] The formation of (**2**) occurs analogously to the addition of methanol to $(Me_3Si)_2N$–P=N–$SiMe_3$, affording $(Me_3Si)_2N$–P(H)(OMe)=N–$SiMe_3$.[13]



Scheme 1. R = Me or $\mathrm{Bu^t}$



Scheme 2. R = Me or $\mathrm{Bu^t}$



Scheme 3.

The lithiated complex $\mathrm{NLiPR(NPCl_2)_2}$ (R = Me or $\mathrm{Bu^t}$) is formed by addition of LiR to the phosph(III)azene moiety of $\mathrm{NP(NPCl_2)_2}$; protonation by propan-2-ol gives (**3**) or (**11**).

It has been mentioned before that treatment with propan-2-ol is essential in order to obtain high yields of organo-substituted cyclophosphazenes. For instance, addition of electrophilic reagents like methyl iodide or allyl bromide instead of propan-2-ol to a 1:1 reaction mixture of (**1**) and LiMe, pre-

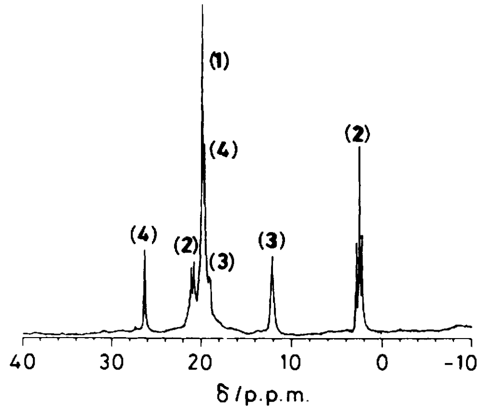
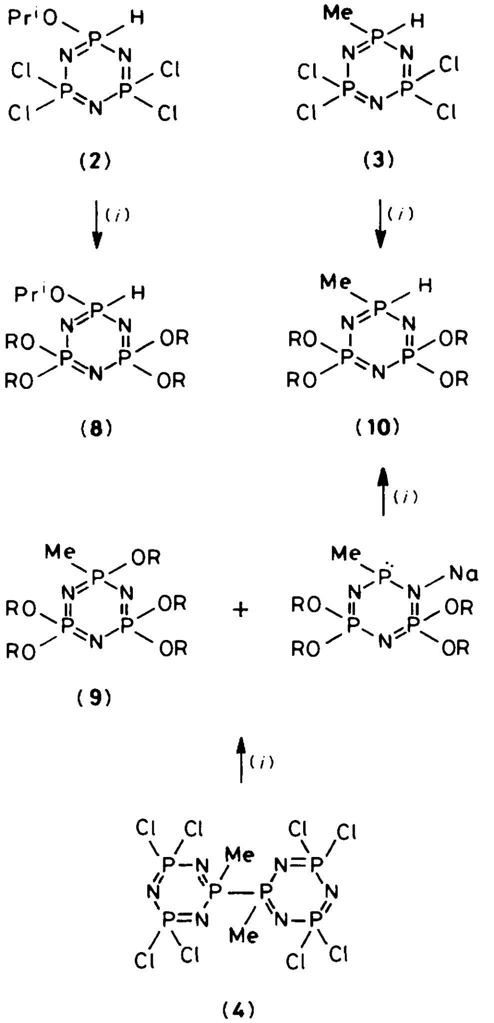


Figure 4. ^{31}P-{^{1}H} N.m.r. spectrum (solvent $CDCl_3$) of the crude reaction mixture of (3), $LiBu^n$, (1), molar ratio 1 : 1 : 1, and propan-2-ol



Scheme 4. (*i*), $Na(OCH_2CF_3)$–$HOCH_2CF_3$; R = CH_2CF_3

dominantly containing $NLiPCl(NPCl_2)_2$ [or $NP(NPCl_2)_2$] induced extensive ring degradation. These results are in striking contrast to the reactions of metallaphosphazenes, as assumed to be generated from (**1**) and [{$CuI(PBu_3)$}$_4$]–MgR^1Cl (R^1 = alkyl), with alkyl iodides R^2I or allyl bromide R^2Br to give $NP(R^1)R^2(NPCl_2)_2$ in excellent yields.[4] Also the reactions of lithiocyclophosphazenes, $NLiPR(NPCl_2)_2$, generated from $NP(H)R(NPCl_2)_2$ and LiMe, with prop-2-ynyl bromide give geminally disubstituted cyclophosphazenes.[15] Hence, a profound difference in nucleophilicity exists between the $=\ddot{P}Cl$ (or $\equiv\ddot{P}$) and $=\ddot{P}R$ moieties.

Analogous to the reactions of (**1**) with Grignard reagents[5] $NLiPMe(NPCl_2)_2$ can be considered as a precursor for the bi(cyclophosphazene) (**4**). Formation of (**4**) in the reaction of (**1**) with two equivalents of LiMe implies the presence of a monosubstituted derivative $NP(Cl)Me(NPCl_2)_2$ (**14**) (Scheme 3). Coupling of $NLiPMe(NPCl_2)_2$ with (**14**) gives (**4**). In principle two possibilities can be suggested for the formation of (**14**), *i.e.* a nucleophilic substitution by LiMe at a PCl_2 centre of (**1**) or a metal–halogen exchange process between $NLiPMe(NPCl_2)_2$ and (**1**). In order to make a proper choice $NLiPMe(NPCl_2)_2$ was generated from (**3**) and $LiBu^n$ and then treated with (**1**) and propan-2-ol. The ^{31}P-{^{1}H} n.m.r. spectrum (Figure 4), which resembles the ^{31}P-{^{1}H} n.m.r. spectrum of the reaction mixture of (**1**) with LiMe, molar ratio 1 : 2, and propan-2-ol with respect to compounds (**2**), (**3**), and (**4**) [Figure 2(*a*)], decides in favour of the metal–halogen exchange process.

$NPMe_2(NPCl_2)_2$ (**5**) is most probably formed according to a nucleophilic substitution reaction by LiMe at the P(Cl)Me centre of (**14**).[7]

It is noteworthy that no other bi(cyclophosphazenes) are formed. Obviously, $NLiPMe(NPCl_2)_2$ prefers to react with (**14**) rather than to couple with (**1**) to give $N_6P_6Cl_9Me$. The absence of the bi(cyclophosphazenes) $N_6P_6Cl_9Me$ and $(N_3P_3Cl_5)_2$ excludes coupling reactions between $NLiPCl(NPCl_2)_2$ [or $NP(NPCl_2)_2$] and (**14**) or (**1**). This means that $NLiPCl(NPCl_2)_2$ [or $NP(NPCl_2)_2$] is less reactive than $NLiPMe(NPCl_2)_2$ towards electrophiles, which has also been concluded from the reactivity of these intermediates towards methyl iodide or allyl bromide.

In the cases of (**6**) and (**7**) it is not possible to give reliable structure assignments beyond the conclusion that both compounds incorporate a $P(H)OPr^i$ moiety. Also reaction of a mixture containing (**2**)—(**7**) with sodium 2,2,2-trifluoroethoxide gave no further indications as only products related to (**2**)—(**4**) were obtained (Scheme 4). Compounds (**2**) and (**3**) were transformed into their 2,2,2-trifluoroethoxy-substituted derivatives (**8**) and (**10**), whereas the P–P bond of (**4**) was cleaved to give (**9**) and (**10**).[12]

Initially, reaction of (**1**) with two equivalents of $LiBu^t$ proceeds according to the same pathway as described for LiMe leading, after treatment with propan-2-ol, to the formation of (**2**), $NP(H)Bu^t(NPCl_2)_2$ (**11**), and $NP(Cl)Bu^t(NPCl_2)_2$ (**12**). However, no bi(cyclophosphazene) was detected, which resembles the reaction of (**1**) with $MgBu^tCl$. Steric hindrance prohibits the coupling reaction of $NLiPBu^t(NPCl_2)_2$ with (**12**).

Compared with LiMe, $LiBu^t$ appeared to be less reactive towards (**1**) as more than two equivalents of $LiBu^t$ were needed to consume all the starting material (**1**). Again steric hindrance due to the Bu^t grouping may be the main cause, assuming that both LiMe and $LiBu^t$ react as solvated monomers.[16] Using three equivalents of $LiBu^t$ no starting material (**1**) was left.

In this context it is noteworthy that $NP(H)Bu^t[NP(OCH_2CF_3)_2]_2$, arising from the reaction of (**11**) with sodium 2,2,2-trifluoroethoxide, is stable in h.p.l.c. experiments. Obviously, the bulky Bu^t grouping protects the hydrido moiety as the analogous Me derivative (**10**) decomposed completely during separation.

Experimental

All experiments were carried out in an atmosphere of dry, oxygen-free nitrogen by applying inert gas–vacuum techniques in combination with Schlenk-type glassware. Liquids were transferred with syringes.

Solvents (thf, diethyl ether and pentane) were distilled prior to use under nitrogen from sodium potassium benzophenone. Propan-2-ol (Merck) was dried over molecular sieves. 2,2,2-Trifluoroethanol (Janssen) was purified by distillation from molecular sieves. A solution of LiMe in diethyl ether (1.6 mol dm^{-3}) was prepared from lithium and methyl chloride according to standard procedures.[17] Solutions of LiBu^{t} in pentane (1.6 mol dm^{-3}) or LiBu^{n} in hexane (1.6 mol dm^{-3}) were obtained commercially from Janssen. Concentrations of the LiR solutions were checked regularly by titration.

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ (**1**) (Otsuka Ltd., Japan) was recrystallized once from n-hexane. The compounds $NP(H)Me(NPCl_2)_2$ (**3**), $(N_3P_3Cl_4Me)_2$ (**4**), and $NP(H)Me[NP(OCH_2CF_3)_2]_2$ (**10**) were prepared according to published methods.[3,5,12]

Purification by h.p.l.c. was carried out using a Waters system consisting of two 6000 A pumps, combined with a R401 RI detector. Separations were performed on Lichrosorb Si 60/10 columns (inside diameter 22 mm, length 30 cm).

^{1}H N.m.r. (60 MHz) spectra were recorded on a Perkin-Elmer R24B instrument using $SiMe_4$ as internal reference; ^{31}P n.m.r. spectra were recorded on a Nicolet NT 200 spectrometer, operating at 81 MHz; $(NPCl_2)_3$ (**1**) was used as external reference (19.9 p.p.m., solution in $CDCl_3$). In all cases the ^{2}H resonance line of the solvent was used for field-frequency lock. Chemical shifts are positive to low field.

Mass spectra were obtained with an AEI Ms9 mass spectrometer (Mr. A. Kiewiet, Department of Organic Chemistry, University of Groningen).

I.r. spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer, using Nujol mulls between KBr discs. Calibration took place by means of polystyrene film band absorptions. I.r. spectra were utilized for fingerprint purposes only [characteristic bands: 1 250—1 150 cm^{-1}, $(NP)_3$ ring].

Elemental analyses were carried out at the Microanalytical Department of this University under the supervision of Mr. A. F. Hamminga.

Analysis of the Crude Reaction Mixtures by N.M.R. Methods.—Reactions of (**1**) (0.5 g, 1.4 mmol) in thf (15 cm^{3}) with LiR, molar ratio 1:1, 1:2 (R = Me or Bu^{t}) or 1:3 (R = Bu^{t}) in diethyl ether (LiMe) (5 cm^{3}) or pentane (LiBu^{t}) (5 cm^{3}) and propan-2-ol (0.54 cm^{3}, 7.0 mmol) were carried out under standard conditions (for a typical reaction procedure see below). All crude reaction mixtures could be dissolved completely in $CDCl_3$ (2.5 cm^{3}). The composition of each reaction mixture was analyzed by ^{31}P n.m.r. (in most cases the ^{1}H n.m.r. spectra appeared to be too complicated). In ^{31}P n.m.r. spectrometry the cyclophosphazenes and hydridocyclophosphazenes differ largely with respect to relaxation times. In order to obtain a reasonable intensity–concentration correlation from the ^{31}P n.m.r. spectra a calibration mixture was prepared, containing three completely characterized analogues of (**2**), (**3**), (**11**) and (**12**), *viz.* NP(H)OPr^{i}(NSOPh)$_2$, NP(H)Bu^{t}(NSOPh)$_2$, and NP(Cl)Bu^{t}(NSOPh)$_2$. We have previously described the preparation of these compounds in a communication.[9] Absolute yields (mol%) as well as total yields of cyclic material are collected in Table 1.

Reactions of $(NPCl_2)_3$ (**1**) *with* LiR, *Molar Ratio* 1:1, 1:2 (R = Me *or* Bu^{t}) *or* 1:3 (R = Bu^{t}), *and Propan-2-ol.*—All reactions were carried out in an identical manner. A typical representative is described below, *i.e.* reaction of (**1**) with LiR, molar ratio 1:2 (R = Me) or 1:3 (R = Bu^{t}), and propan-2-ol. LiMe (34 mmol) in diethyl ether (50 cm^{3}) or LiBu^{t} (51 mmol) in pentane (50 cm^{3}) was added dropwise to a stirred solution of (**1**) (6.0 g, 17 mmol) in thf (180 cm^{3}) at −78 °C. The reaction mixture turned yellow. After stirring for 2 h at −60 °C propan-2-ol (6.5 cm^{3}, 85 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature within 1.5 h. Removing the solvent by evaporation and extraction of the remainder with two portions of pentane (50 cm^{3}) afforded a colourless oil [4.4 g (R = Me), 5.4 g (R = Bu^{t})].

Reactions with $Na(OCH_2CF_3)$.—A solution of the reaction mixture described above in thf (40 cm^{3}) was added dropwise to a stirred solution of sodium 2,2,2-trifluoroethoxide, prepared from sodium [1.8 g, 78 mmol (R = Me); 2.7 g, 117 mmol (R = Bu^{t})] and 2,2,2-trifluoroethanol [20.6 cm^{3}, 180 mmol (R = Me); 30.9 cm^{3}, 240 mmol (R = Bu^{t})] at 0 °C, in thf (120 cm^{3}) at 0 °C. Stirring was continued for 24 h at 0 °C, after which the reaction mixture was poured into water (200 cm^{3}) and diethyl ether (100 cm^{3}). After separation of the organic layer the water was again extracted with diethyl ether (100 cm^{3}). After drying the combined organic layers on anhydrous magnesium sulphate, the solvent was removed under reduced pressure, yielding a colourless oil [7.5 g (R = Me), 5.1 g (R = Bu^{t})]. Filtration of a solution of this oil in dichloromethane through neutral alumina and evaporation of the solvent afforded a colourless liquid [5.0 g (R = Me), 3.5 g (R = Bu^{t})], which was analyzed by ^{31}P n.m.r. (Table 2). Both crude reaction mixtures were chromatographed by h.p.l.c. using hexane–thf (95:5) as eluant.

In the case of LiMe two fractions were isolated.

Fraction 1: 2.23 g; molecular distillation (70 °C at 0.1 mmHg) afforded a colourless liquid (2.0 g, 20%), NP(H)OPr^{i}[NP(OCH$_2$CF$_3$)$_2$]$_2$ (**8**) [Found: C, 22.60; H, 2.65; N, 7.20. $C_{11}H_{16}F_{12}N_3O_5P_3$ (*M* = 591.21) requires C, 22.35; H, 2.75; N, 7.10%]. Mass spectrum: *m/e* 591 (M^+, 5%), 550 ($M - C_3H_5$, 100%), 532 (M − OPr^{i}, 60%). ^{1}H N.m.r. ($CDCl_3$): δ 1.3 [6 H, d, ^{3}J(HH) 5.8 Hz, Me], 4.2 (8 H, m, CH$_2$), 4.5 (1 H, m, CH), 6.4 [1 H, d of m, ^{1}J(PH) 637 Hz, PH].

Fraction 2: 1.19 g; molecular distillation (70 °C at 0.1 mmHg) afforded a colourless liquid (1.0 g, 9%), NP(Me)OCH$_2$CF$_3$-[NP(OCH$_2$CF$_3$)$_2$]$_2$ (**9**) [Found: C, 20.35; H, 2.05; N, 6.50. $C_{11}H_{13}F_{15}N_3O_5P_3$ (*M* = 645.18) requires C, 20.50; H, 2.05; N, 6.50%]. Mass spectrum: *m/e* 645 (M^+, 79%), 626 (M − F, 58%), 546 ($M - OCH_2CF_3$, 54%), 532 [$M - (OCH_2CF_3 + CH_2)$, 100%]. ^{1}H N.m.r. ($CDCl_3$): δ 1.7 [3 H, d, ^{2}J(PH) 16.8 Hz, Me], 4.3 (10 H, m, CH$_2$).

In the case of LiBu^{t} two fractions were also isolated.

Fraction 1: 0.9 g; molecular distillation (70 °C at 0.1 mmHg) gave a colourless oil (0.6 g, 6%), which solidified after standing overnight, NP(H)Bu^{t}[NP(OCH$_2$CF$_3$)$_2$]$_2$ (**13**) [Found: C, 24.40; H, 3.00; N, 7.05. $C_{12}H_{18}F_{12}N_3O_4P_3$ (*M* = 589.24) requires C, 24.45; H, 3.10; N, 7.15%]. Mass spectrum could not be obtained due to thermal decomposition. ^{1}H N.m.r. ($CDCl_3$): δ 1.1 [9 H, d, ^{3}J(PH) 19.3 Hz, Bu^{t}], 4.2 (8 H, m, CH$_2$), 6.7 [1 H, d, of t, ^{1}J(PH) 527, ^{3}J(PH) 5.0 Hz, PH]. The low yield of (**13**), which appeared to be the predominant reaction product is probably due to partial decomposition during the h.p.l.c. experiment.

Fraction 2: 1.1 g, molecular distillation (70 °C at 0.1 mmHg) gave a colourless liquid (0.8 g, 8%), NP(H)OPr^{i}[NP(OCH$_2$CF$_3$)$_2$]$_2$ (**8**).

Reaction of $NP(H)Me(NPCl_2)_2$ (**3**) *with* LiBu^{n}, $(NPCl_2)_3$ (**1**), *and Propan-2-ol.*—LiBu^{n} (1.6 mmol) in pentane (5 cm^{3}) was added dropwise to a stirred solution of (**3**) (0.46 g, 1.6 mmol) in thf (15 cm^{3}) at −78 °C. Stirring was continued for 0.8 h at −60 °C, after which (**1**) (0.55 g, 1.6 mmol) in thf (10 cm^{3}) was added dropwise. Stirring was continued for 2 h at −60 °C. After addition of propan-2-ol (0.54 cm^{3}, 7.0 mmol) the reaction mixture was allowed to warm to room temperature within 1.5 h.

The solvent was removed by evaporation and the remainder extracted with two portions of pentane (10 cm^3) affording an oily substance (0.84 g), which was analyzed by ^{31}P n.m.r. spectrometry (Figure 4). The mixture contained $(NPCl_2)_3$ (**1**) (35%), $NP(H)OPr^i(NPCl_2)_2$ (**2**) (25%), $(N_3P_3Cl_4Me)_2$ (**4**) (25%), and $NP(H)Me(NPCl_2)_2$ (**3**) (15%).

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