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A propene-substituted cyclotriphosphazene: synthesis, characterization and polymerization

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The elimination reaction of the sulfonium-substituted chlorocyclotriphosphazene $N_3P_3Cl_4Pr^i(CMe_2OSO_2Me)$ with 1,8-diazabicyclo[5.4.0]undec-7-ene afforded a new olefin-substituted chlorocyclotriphosphazene, $N_3P_3Cl_4Pr^i(CMe{=}CH_2)$, and an *ansa* derivative with formula $N_3P_3Cl_3Pr^i(CMe_2CH{=}CMeO)$. The crystal structures of the three compounds were determined. The sequence of N−P bond lengths in the molecules can be explained from the difference in group electronegativity of the phosphorus centres. For $N_3P_3Cl_4Pr^i(CMe_2OSO_2Me)$ two crystallographic independent molecules are present in the asymmetric unit. In $N_3P_3Cl_3Pr^i(CMe_2CH{=}CMeO)$ the bridge between two phosphorus atoms compresses the inorganic ring, which is reflected in a large deviation of 0.563(2) Å of one of the N atoms from the least-squares plane through the remaining ring atoms. This distortion is accompanied by a contraction of the non-bonded $P\cdots P$ distances. The propene derivative has been used in radical copolymerization with methyl methacrylate and styrene. A maximum incorporation of 18 mol % was achieved with styrene as comonomer.

Chlorocyclophosphazenes are reactive species. The chloro atoms can be replaced in substitution reactions with a large variety of nucleophiles. Following this synthetic strategy a number of cyclophosphazene derivatives with one or more unsaturated side groups have been prepared.[1,2] These compounds are of interest as they can serve as precursors for the synthesis of hybrid inorganic–organic polymers. The properties of these systems can be controlled by introducing the inorganic component into the organic polymer. In this way special polymers have been synthesized suitable for application as *e.g.* flame retardants or photoresists.[3–5]

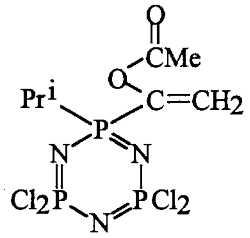
When the double bond is separated by a spacer from the bulky electron-withdrawing inorganic ring the radical polymerization behaviour resembles that of the analogous organic monomer in most cases.[1,2] However, if the phosphazene ring is directly bonded to the double bond the reactivity of the vinyl group is significantly influenced by it.[2,6] For instance, the vinyl acetate derivative **1** is not able to undergo homopolymerization whereas vinyl acetate is.[6]

This paper describes the synthesis and characterization of a propene-substituted chlorocyclophosphazene which has the unsaturated group attached to the inorganic ring by a direct phosphorus–carbon bond. The substituents on the double bond cause steric and electronic perturbations of the olefin moiety. By investigating the behaviour of the novel monomer in radical polymerization reactions one can observe to what extent these perturbations influence the reactivity of the olefin. The reactivity of this propene derivative in radical copolymerization reactions with styrene and methyl methacrylate (mma) are described.

Experimental

Measurements

The NMR spectra were recorded on a Varian Gemini-200 spectrometer operating at 199.98 (^1H), 50.29 (^{13}C) and 80.95 (^{31}P) MHz with $CDCl_3$ as internal standard for ^1H and ^{13}C and $(NPCl_2)_3$ in $CDCl_3$ as external reference for ^{31}P. Gel permeation chromatography measurements were performed on a Spectra-Physics AS 1000 system equipped with a Viscotek H502 viscometer and a Shodex RI-71 refractive-index detector coupled to a Dawn (MALLS) light-scattering apparatus; $CHCl_3$ or tetrahydrofuran (thf) was used as eluent. The columns were calibrated with polystyrene standards. Glass transition temperatures were recorded by using a Perkin-Elmer DSC7 unit. The measurements were carried out at a heating rate of 10 °C min^{-1}. Thermogravimetric analyses were obtained with a Perkin-Elmer TGA-7 thermogravimetric analyser at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. Elemental analyses were carried out at the Microanalytical Department of the University of Groningen. Copolymer compositions were determined from the weight percentage of chlorine or ^1H NMR spectra.



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Materials and procedures

All reactions were carried out in an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Hexachlorocyclotriphosphazene **2** was kindly provided by Shin Nisso Kako Co. and purified by recrystallization from hexane (Merck). *gem*-Tetrachloro-2-(1-hydroxy-1-methylethyl)-2-isopropylcyclotriphosphazene **3** was synthesized according to the literature.[7] Methyl methacrylate (Janssen) and styrene (Janssen) were distilled from calcium hydride–copper bronze under nitrogen at reduced pressure and stored at −20 °C. Triethylamine (Merck) was dried over KOH and distilled from KOH under nitrogen. 2,2′-Azobisisobutyronitrile (aibn, Janssen) was recrystallized from methanol and stored under nitrogen at 5 °C. Acetonitrile (Janssen) was dried over 3 Å molecular sieves (Merck). Diethyl ether (Janssen) was distilled from $CaCl_2$ and stored over sodium wire. All other reagents and solvents were used as received.

Syntheses

$N_3P_3Cl_4Pr^i(CMe_2OSO_2Me)$ 4. To a stirred solution of compound **3** (3.8 g, 10.0 mmol) and methanesulfonyl chloride (2.2 cm^3, 28.4 mmol) in diethyl ether (25 cm^3) was added slowly NEt_3 (4 cm^3, 28.8 mmol). After stirring for half an hour at room temperature the solution was refluxed for 2 h and filtered to remove the precipitated salts. After filtration the ether was washed with water (20 cm^3) and the water layer was in return extracted twice with ether (10 cm^3). The combined ether layers were dried on $MgSO_4$, filtered and stirred with activated carbon. The ether was evaporated under reduced pressure and yielded a light yellow oil (3.37 g, 73%) which crystallized on standing. Recrystallization from pentane resulted in a white solid with m.p. 79.0–80.5 °C (Found: C, 18.7; H, 3.5; Cl, 31.05; S, 7.05. $C_7H_{16}Cl_4N_3O_3P_3S$ requires C, 18.4; H, 3.55; Cl, 31.05; S, 7.0%). $\delta_H(CDCl_3)$ 1.29 (6 H, dd, $^3J_{PH}$ 19.0, $^3J_{HH}$ 7, CH_3), 1.93 (6 H, d, $^3J_{PH}$ 15.6, CH_3), 2.3 (1 H, m, CH) and 3.1 (3 H, s, CH_3); $\delta_C(CDCl_3)$ 16.1 (CH_3), 22.1 (CH_3), 26.7 (d, $^1J_{PC}$ 88.1, CH), 41.1 (SCH_3) and 89.4 (d, $^1J_{PC}$ 108.1 Hz, C); $\delta_P(CDCl_3)$ 19.4 (PCl_2) and 46.1 (PC), A_2B type, $^2J_{PP}$ unresolved.

$N_3P_3Cl_4Pr^i(CMe{=}CH_2)$ 5. A solution of compound **4** (2.2 g, 4.8 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) (1.5 cm^3, 10 mmol) in acetonitrile (15 cm^3) was refluxed for 27 h. After removal of the solvent *in vacuo*, diethyl ether (75 cm^3) was added. The ether solution was washed with water (20 cm^3) and the water layer was extracted twice with ether (50 cm^3). The combined ether layers were dried over $MgSO_4$, filtered and stirred with activated carbon. The ether was evaporated under reduced pressure and the crude product purified by flash chromatography (silica gel 230–400 mesh; eluent hexane–thf, 9 : 1) to yield a light yellow oil, which became a solid after some time. The ^{31}P NMR spectrum showed that the crude product was composed of compounds **5** (about 95% of the total peak area) and **6** (about 5%). The two were separated by flash chromatography (silica gel 230–400 mesh; eluent hexane–thf, 9 : 1). Recrystallization from pentane yielded a white solid (0.63 g, 36%) with m.p. 48.5–50.5 °C (Found: C, 20.25; H, 3.4; Cl, 39.2. $C_6H_{12}Cl_4N_3P_3$ requires C, 19.95; H, 3.35; Cl, 39.3%). $\delta_H(CDCl_3)$ 1.14 (6 H, dd, $^3J_{PH}$ 19.6, $^3J_{HH}$ 7.1, CH_3), 1.98 (3 H, d, $^3J_{PH}$ 13.6, CH_3), 2.0 (1 H, m, CH), 5.85 (1 H, d, $^3J_{PH,trans}$ 44.0, $=CH_2$) and 5.97 (1 H, d, $^3J_{PH,cis}$ 21.5, $=CH_2$); $\delta_C(CDCl_3)$ 14.1 (CH_3), 17.9 (d, $^2J_{PC}$ 13.1, CH_3), 27.5 (dt, $^1J_{PC}$ 92.7, $^3J_{PC}$ 4, CH), 129.6 (d, $^2J_{PC}$ 9.1, $=CH_2$) and 136.6 (dd, $^1J_{PC}$ 109.8, $^3J_{PC}$ 3 Hz, C=); $\delta_P(CDCl_3)$ 18.2 (PCl_2) and 40.2 (PC), A_2B type, $^2J_{PP}$ unresolved.

$N_3P_3Cl_3Pr^i(CMe_2CH{=}CMeO)$ 6. Recrystallization of **6** from pentane gave a pure compound with m.p. 109.0–110.5 °C (Found: C, 28.55; H, 4.7; Cl, 27.35. $C_9H_{17}Cl_3N_3OP_3$ requires C, 28.25; H, 4.5; Cl, 27.8%). $\delta_H(CDCl_3)$ 1.24 (3 H, dd, $^3J_{PH}$ 19.6, $^3J_{HH}$ 7.0, $CHCH_3$), 1.29 (3 H, dd, $^3J_{PH}$ 18.1, $^3J_{HH}$ 7.1, $CHCH_3$), 1.33 (3 H, d, $^3J_{PH}$ 15.9, CCH_3), 1.49 (3 H, d, $^3J_{PH}$ 15.2, CCH_3), 1.92 (3 H, m, CH_3), 2.1 (1 H, m, CH) and 4.82 (1 H, m, CH); $\delta_C(CDCl_3)$ 16.1 ($CHCH_3$), 16.5 ($CHCH_3$), 23.1 (CH_3), 23.9 (CH_3), 25.0 (CH_3), 25.8 (d, $^1J_{PC}$ 93.6, CH), 44.0 (d, $^1J_{PC}$ 72.7, C), 120.4 ($=CH_2$) and 148.0 (d, $^2J_{PC}$ 10.0 Hz, C=); $\delta_P(CDCl_3)$ AXY type with multiplets at 51.8 and 24.5.

Attempted homopolymerization of compound 5

To compound **5** (0.198 g, 0.549 mmol) was added 1 mol % aibn. The sample was flushed three times with nitrogen and placed in an oil-bath at 55 ± 2 °C for 2 d. After another 1 mol % aibn had been added, the solution was stirred for 20 h. The ^{31}P NMR spectrum of the resultant brown viscous oil showed no resonance signals of ring products other than **5**.

Copolymerization of compound 5

With styrene. A typical procedure is as follows. To a solution of compound **5** (0.298 g, 0.826 mmol) in styrene (855 μl, 7.46 mmol) was added 1 mol % of aibn. After three freeze-pump-thaw cycles the sample was placed in an oil-bath at 55 ± 2 °C for 66 h. The reaction mixture was diluted with dichloromethane and precipitated in excess of methanol. The polymer was collected by centrifugation, dissolved in dichloromethane and reprecipitated in methanol. The white powdery polymer was filtered off, washed and vacuum dried. Yield 0.59 g (55%) (Found: Cl, 5.55%). $\delta_P(CDCl_3)$ 16.4 (PCl_2) and 57.5 (PC), A_2B type, $^2J_{PP}$ unresolved. Composition and conversion data are summarized in Table 6.

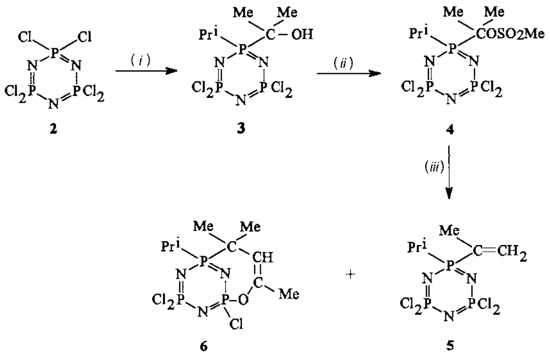
With mma. The copolymerization reactions were conducted in a similar way as described above. Composition and conversion data are summarized in Table 6.

Crystallography

Transparent colourless crystals of compounds **4**–**6** were used for characterization and data collection. The crystals were glued on a top of a glass fibre, and cooled to 130 K by using an on-line liquid-nitrogen cooling system mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a MicroVAX-2000 computer.[8] Unit-cell dimensions and the orientation matrix were determined from a least-squares treatment of the setting angles of 22 reflections with $16.52 < \theta < 18.93$ (**4**), $16.59 < \theta < 20.83$ (**5**) and $17.97 < \theta < 20.57°$ (**6**).[9] The space group was derived from the systematic absences. Reduced cell calculations did not indicate any higher metric lattice symmetry and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[10–12] Crystal and/or instrumental instability was monitored by measurement of the intensities of three reference reflections which were collected after every 3 h of X-ray exposure time. In all cases the fluctuations during data collection were not larger than those expected from Poisson statistics. Intensity data were corrected for Lorentz-polarization effects and scale variation, but not for absorption. Variances were calculated based on counting statistics and the term (P^2I^2) where P is the instability constant as derived from the excess variance in the reference reflections.[13] Equivalent reflections were averaged and regarded as observed if satisfying the $I \geqslant 2.5\sigma(I)$ criterion. Pertinent numerical data on the structure determinations are given in Table 2.

The structures of compounds **5** and **6** were solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[14] The structure of **4** was solved by direct methods with SHELXS 86.[15] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ), minimizing the function $Q = \Sigma_h[w(|F_o| - k|F_c|)^2]$.[16] A subsequent Fourier-difference synthesis resulted in the location of all the hydrogen atoms, the coordinates and isotropic thermal displacement parameters of which were refined. Final refinements on F were carried out by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms. For compound **4** the final Fourier-difference map was essentially featureless with the highest peaks in the vicinity of the chlorine atoms. The Fourier-difference maps for **5** and **6** did not show any significant residual features, except for a small peak of 1.22 e $Å^{-3}$ in the vicinity of the O(1) position in **6**.

Selected molecular geometry data are collected in Tables 3–5. Neutral atom scattering factors were taken from Cromer and Mann.[17] Anomalous dispersion factors were taken from Cromer and Liberman[18] and included in F_c. All calculations were carried out on a HP9000/735 computer at the University of Groningen with the program packages XTAL, SHELXL (least-square refinements) and PLATON (calculation of geometric data).[19–21]



Scheme 1 Reaction scheme for the synthesis of compound **5**. (*i*) $MgPr^iCl$, $[\{CuI(PBu^n_3)\}_4]$ then Me_2CO; (*ii*) $ClSO_2Me$; (*iii*) dbu

Table 1 Selected olefin ^{13}C chemical shifts (δ)

Compound	C=	=CH$_2$
1	148.2	119.2
5	136.6	129.6
$N_3P_3F_5(CMe{=}CH_2)$	134.1	131.6
Vinyl acetate	141.8	96.8
Styrene	136.9	113.7
mma	136.9	124.7

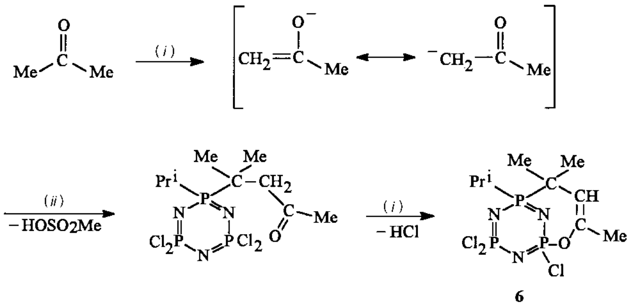
Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/455.

Results and Discussion

The propene derivative **5** was synthesized according to Scheme 1. The first step involves the synthesis of the well known tetrachloro-2-(1-hydroxy-1-methylethyl)-2-isopropylcyclotriphosphazene **3** *via* the reaction of a phosphazenoylcuprate and acetone.[7] Dehydration of this alcohol derivative can afford the desired propenylcyclophosphazene **5**. A large number of procedures have been described for the conversion of alcohols into olefins of which some require the use of a dehydrating agent such as $KHSO_4$, KOH or anhydrous $CuSO_4$.[22–24] Secondary and tertiary alcohols are also dehydrated on refluxing in $P(NMe_2)_3$.[25] This last method is however not applicable for **3** as dimethylamine is formed during the dehydration reaction which can react with the PCl_2 groups.[26,27]

Attempts to prepare compound **5** *via* the direct thermal dehydration of **3** were only partly successful. The ^{31}P NMR spectra of the reaction mixtures showed that only small amounts of the propene derivative (resonances at δ 18.2 and 40.2) were formed. The major fraction appeared to be starting material (δ 18.6 and 50.3), together with an unknown compound with resonances at δ 17.7 and 56.5. A small amount of the latter is also present in the reaction mixture after the first step. No attempts were made to isolate this product.

The low yields of propenylcyclophosphazene obtained with this direct method prompted us to transform the hydroxyl group into a better leaving group. Reaction of compound **3** with methanesulfonyl chloride yields $(NPCl_2)_2NPPr^i(CMe_2OSO_2Me)$ **4**. Subsequent elimination of the sulfonium group on refluxing in acetonitrile in the presence of the base dbu proceeds smoothly to give $(NPCl_2)_2NPPr^i(CMe{=}CH_2)$ **5**. In the ^{13}C NMR spectrum of **5** a large downfield shift to δ 129.6 is observed for the absorption of the β-carbon of the vinyl group. For **1** the $\delta(^{13}C)({=}CH_2)$ is 119.2 (Table 1) which reflects the larger electron-donating ability of the acetoxy substituent as the phosphazene group is identical in both compounds.[28] For the compound $N_3P_3F_5(CMe{=}CH_2)$ a β-carbon shift of δ 131.6 has been reported, which is close to the value of **5**.[29]



Scheme 2 Proposed mechanism for the formation of compound **6**. (*i*) dbu; (*ii*) compound **4**

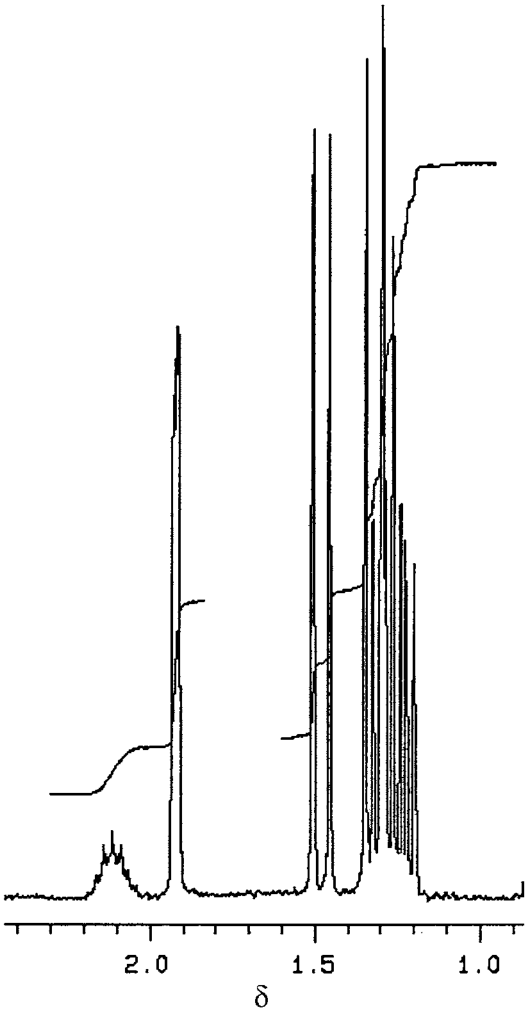


Fig. 1 The alkyl region in the ^1H NMR spectrum of compound **6**

Apart from the expected propene derivative a small quantity of another compound was present in the reaction mixture. This appeared to be an *ansa* derivative. In the ^{31}P NMR spectra of the crude reaction mixtures no resonance signals of compounds other than **4**–**6** are detected. The formation of **6** is not observed during the thermal dehydration reaction of **3**. The underlying reaction pathway leading to the formation of **6** is believed to involve reaction of acetone with **4**. A tentative mechanism is shown in Scheme 2. The origin of traces of acetone in the reaction mixture might be the result of some hydrolysis of **4**. On the other hand, however, addition of acetone to the reaction mixture does not lead to a higher yield of **6**.

Examination of the ^1H NMR spectrum of compound **6** (Fig. 1) reveals that the two methyl groups [C(2) and C(3)] of the isopropyl substituent are not magnetically equivalent. Whereas

Table 2 Crystallographic data for compounds **4–6** and details of structure determination *

	4	**5**	**6**
Chemical formula	$C_7H_{16}Cl_4N_3O_3P_3S$	$C_6H_{12}Cl_4N_3P_3$	$C_9H_{17}Cl_3N_3OP_3$
M	457.02	360.91	382.53
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	7.974(1)	8.351(1)	11.772(1)
b/Å	14.311(2)	17.366(1)	11.092(1)
c/Å	17.875(3)	11.214(1)	13.416(1)
α/°	113.37(1)		
β/°	96.50(1)	110.242(5)	110.873(7)
γ/°	93.56(1)		
U/Å^3	1847.6(5)	1526.0(2)	1636.8(2)
D_c/g cm^{-3}	1.643	1.571	1.552
F(000)	928	728	784
μ(Mo-Kα)/cm^{-1}	10.2	10.70	8.46
Data: total, unique	7772, 7222	4094, 3488	4304, 3928
Data observed [$I \geqslant 2.5\sigma(I)$]	6261	2749	3631
$R1$ [$=\Sigma(I - \bar{I})/\Sigma I$)]	0.011	0.014	0.017
$R2$ ($=\Sigma\sigma/\Sigma I$)	0.034	0.031	0.015
Refined parameters	508	193	240
R,R'	0.036, 0.038	0.038, 0.042	0.030, 0.032
Residual electron density in final Fourier-difference map/e Å^{-3}	−1.07, 1.17	−0.60, 0.68	−0.41, 0.48
Crystal size/mm	0.16 × 0.19 × 0.20	0.12 × 0.14 × 0.26	0.18 × 0.25 × 0.50

* Details in common: $Z = 4$; λ(Mo-Kα) 0.710 73 Å; $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R' = [\Sigma(w|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$; $w = 1$.

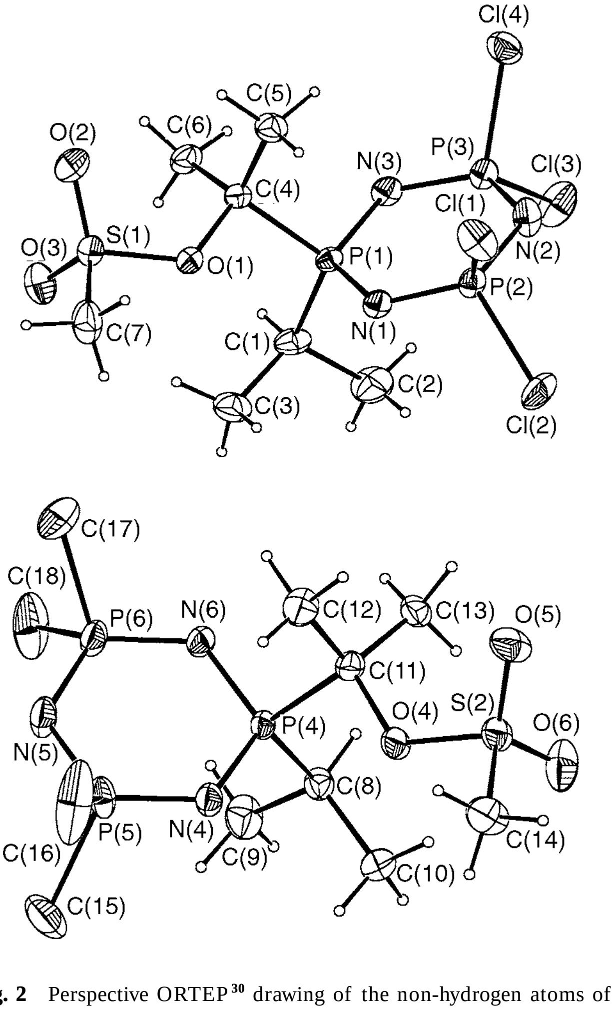


Fig. 2 Perspective ORTEP[30] drawing of the non-hydrogen atoms of compound **4** with the atom labelling scheme for the non-hydrogen atoms. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density; the hydrogen atoms are drawn with an arbitrary radius

for similar phosphazene compounds with an isopropyl ligand only one double doublet is observed due to P–H ($^3J_{PH}$) and H–H ($^3J_{HH}$) coupling, the methyl groups in **6** appear as two partly overlapping double doublets (δ 1.24 and 1.29). The inequivalence of C(2) and C(3) is also manifest in the proton-decoupled ^{13}C NMR spectrum where two resonance signals at δ 16.1 and 16.5 are found. The observed inequivalence can be explained from the fact that the isopropyl group is attached to an asymmetrical phosphorus atom [P(1)]. As a result the two methyl groups are diastereotopic. The C(5) and C(6) methyl groups are also magnetically inequivalent and appear as two separate doublets at δ 1.33 and 1.49 ($^3J_{PH}$ 15.9 and 15.2 Hz, respectively) in the ^{1}H NMR spectrum and as two singlets in the ^{13}C NMR spectrum.

Crystal structures of compounds 4 and 5

For compound **4** two crystallographic independent molecules are present in the asymmetric unit. The six-membered cyclophosphazene ring in both **4** and **5** is almost planar (Figs. 2 and 3). In the case of **4** the largest deviation from the least-squares plane through the inorganic P–N ring is observed for one of the phosphorus atoms with a mean value of 0.037(1) Å. For **5** the largest deviation from the least-squares plane through P(1), N(1), P(2), N(2), P(3) and N(3) is 0.079(3) Å for the atom N(1).

The distribution of N–P bond lengths in compounds **4** and **5** is identical and follows the same sequence as observed for **1**.[28] Again the largest and smallest values are found in the segment PR_2–N–PCl_2 for the N–PR_2 bond [σ-weighted average for **4** being 1.615(3) Å and for **5** at 1.621(2) Å] and for N–PCl_2 [σ-weighted average for **4** being 1.560(2) Å and for **5** 1.549(2) Å], respectively. In the segment PCl_2–N–PCl_2 the N–P distances are equal [σ-weighted average for **4** being 1.586(3) Å and for **5** 1.579(2)Å] and intermediate between those in the segment PR_2–N–PCl_2 (Table 3).

Just as was found for the endocyclic bond lengths, the endocyclic bond angles are equal within experimental error for both molecules with σ-weighted average values of 115.2(1) (N–PR_2–N), 119.95(8) (N–PCl_2–N), 122.3(2) (PR_2–N–PCl_2) and 119.7(1)° (PCl_2–N–PCl_2). These values are comparable with those observed for compound **1**.[28] The same holds for the exocyclic Cl–P–Cl bond angles with a σ-weighted average value of 100.3(2)°. On the other hand the exocyclic C–P–C bond angle of 108.5(2)° in **5** is somewhat smaller than that of **4** [110.7(4)°]. This is probably caused by a slightly increased steric hindrance of the larger substituents on the phosphorus atom of the latter.

Table 3 Selected bond lengths (Å) and angles (°) of compound **4** with their estimated standard deviations (e.s.d.s) in parentheses

Residue 1		Residue 2	
Cl(1)–P(2)	2.0086(14)	Cl(5)–P(5)	2.007(2)
Cl(2)–P(2)	2.0005(13)	Cl(6)–P(5)	1.985(2)
Cl(3)–P(3)	2.0101(12)	Cl(7)–P(6)	2.005(2)
Cl(4)–P(3)	1.9973(12)	Cl(8)–P(6)	1.996(2)
P(1)–C(1)	1.807(3)	P(4)–C(8)	1.806(3)
P(1)–C(4)	1.849(3)	P(4)–C(11)	1.859(3)
P(1)–N(1)	1.613(3)	P(4)–N(4)	1.607(3)
P(1)–N(3)	1.618(3)	P(4)–N(6)	1.621(3)
P(2)–N(1)	1.554(3)	P(5)–N(4)	1.558(3)
P(2)–N(2)	1.585(3)	P(5)–N(5)	1.589(3)
P(3)–N(2)	1.591(3)	P(6)–N(5)	1.577(3)
P(3)–N(3)	1.560(3)	P(6)–N(6)	1.566(3)
N(1)–P(1)–N(3)	115.18(14)	N(4)–P(4)–N(6)	115.7(2)
N(1)–P(2)–N(2)	120.07(15)	N(4)–P(5)–N(5)	119.6(2)
N(2)–P(3)–N(2)	119.81(14)	N(5)–P(6)–N(6)	120.1(2)
P(1)–N(1)–P(2)	122.8(2)	P(4)–N(4)–P(5)	122.6(2)
P(1)–N(3)–P(3)	122.4(2)	P(4)–N(6)–P(6)	121.7(2)
P(2)–N(2)–P(3)	119.4(2)	P(5)–N(5)–P(6)	119.9(2)
C(1)–P(1)–C(4)	111.09(15)	C(8)–P(4)–C(11)	110.27(14)
Cl(1)–P(2)–Cl(2)	100.21(6)	Cl(5)–P(5)–Cl(6)	100.62(7)
Cl(3)–P(3)–Cl(4)	100.10(5)	Cl(7)–P(6)–Cl(8)	100.66(6)
Torsion angles			
N(3)–P(1)–N(1)–P(2)	0.8(2)	N(6)–P(4)–N(4)–P(5)	5.2(3)
N(1)–P(1)–N(3)–P(3)	3.9(2)	N(4)–P(4)–N(6)–P(6)	−4.3(2)
N(2)–P(2)–N(1)–P(1)	−2.5(3)	N(5)–P(5)–N(4)–P(4)	−1.5(3)
N(1)–P(2)–N(2)–P(3)	−0.3(3)	N(4)–P(5)–N(5)–P(6)	−3.3(3)
N(3)–P(3)–N(2)–P(2)	4.8(3)	N(6)–P(6)–N(5)–P(5)	4.1(3)
N(2)–P(3)–N(3)–P(1)	−6.7(3)	N(5)–P(6)–N(6)–P(4)	−0.2(3)

Table 4 Selected bond lengths (Å) and angles (°) of compound **5** with their e.s.d.s in parentheses

Cl(1)–P(2)	1.9983(13)	P(2)–N(2)	1.577(3)
Cl(2)–P(2)	1.9925(15)	P(3)–N(2)	1.581(3)
Cl(3)–P(3)	2.0023(14)	P(3)–N(3)	1.549(3)
Cl(4)–P(3)	2.0077(12)	P(1)–C(1)	1.807(5)
P(1)–N(1)	1.622(3)	P(1)–C(4)	1.788(4)
P(1)–N(3)	1.620(3)	C(4)–C(6)	1.319(8)
P(2)–N(1)	1.549(3)		
N(1)–P(1)–N(3)	115.2(2)	P(1)–N(3)–P(3)	122.2(2)
N(1)–P(2)–N(2)	120.0(2)	C(1)–P(1)–C(4)	108.5(2)
N(2)–P(3)–N(3)	120.0(2)	Cl(1)–P(2)–Cl(2)	99.16(6)
P(1)–N(1)–P(2)	121.7(2)	Cl(3)–P(3)–Cl(4)	99.98(6)
P(2)–N(2)–P(3)	119.7(2)		
Torsion angles			
N(3)–P(1)–N(1)–P(2)	10.6(3)	N(1)–P(2)–N(2)–P(3)	6.3(3)
N(1)–P(1)–N(3)–P(3)	−1.1(3)	N(3)–P(3)–N(2)–P(2)	3.0(3)
N(2)–P(2)–N(1)–P(1)	−13.4(3)	N(2)–P(3)–N(3)–P(1)	−5.4(3)

Crystal structure of compound 6

For the inorganic ring of the derivative **6** it is noted that there are three different phosphorus centres present instead of two in the rings of the aforementioned molecules (Fig. 4). The sequence of N–P bond lengths resulting from this geometry can again be explained by considering the electronegativity of the phosphorus centres. As $\chi(PCl_2) > \chi(PClR) > \chi(PR_2)$, the longest and shortest N–P bonds are predicted to be the N–PR$_2$ and N–PCl$_2$ respectively in the segment PR$_2$–N–PCl$_2$.[31–34] Indeed a largest value of 1.627(2) Å is found for the N(1)–P(1) distance, while the smallest value at 1.565(2) Å is found for the N(1)–P(2) distance. In the segment PR$_2$–N–PClR the bond lengths are comparable with those in the segment PR$_2$–N–PCl$_2$. The smallest difference in N–P bond lengths is found in the segment PClR–N–PCl$_2$ where the difference in electronegativity between the phosphorus centres is also the smallest. Here the N–PClR length is 1.595(2) Å and N–PCl$_2$ 1.586(2) Å.

Although the presence of a bridge between the phosphorus atoms P(1) and P(3) does not affect the bond lengths in the inorganic ring, it does have a marked influence on the geometry of the cyclotriphosphazene ring. The most distinct observations are the more equatorial positions of the substituents on P(1) and P(3) with respect to the chlorine atoms on P(C) and the loss of planarity of the PN ring. Atom N(3) is situated 0.563(2) Å outside the least-squares plane formed by P(1), N(1), P(2), N(2) and P(3). This distortion is probably the result of the strain induced by the bridge between the phosphorus atoms P(1) and P(3). A similar configuration is observed for other bridged cyclotriphosphazene derivatives.[35] Comparison of the data reveals that there seems to be a relationship between the length of the loop and the deviation of the nitrogen atom enclosed by the bridged P atoms from the plane of the remaining ring atoms. For instance, for the molecules **6**–**8** this deviation is 0.4 Å for **7**, whereas the inorganic ring of **8** shows no significant deviation from planarity.[35,36]

The compression of the inorganic ring is also reflected by the contraction of the non-bonded P···P distances (y, y', y''). In $(NPCl_2)_3$ this distance is 2.746(2) Å while for compound **6** y has a normal value of 2.7508(9) Å, y' is shortened to 2.716(1) Å

Table 5 Selected bond lengths (Å) and angles (°) of compound **6** with their e.s.d.s in parentheses

Cl(1)–P(2)	2.0139(8)	P(3)–N(3)	1.573(2)
Cl(2)–P(2)	2.0199(8)	P(1)–C(1)	1.809(2)
Cl(3)–P(3)	1.9851(8)	P(1)–C(4)	1.837(2)
P(1)–N(1)	1.627(2)	P(3)–O(1)	1.596(2)
P(1)–N(3)	1.621(2)	C(4)–C(7)	1.529(3)
P(2)–N(1)	1.565(2)	C(7)–C(8)	1.335(3)
P(2)–N(2)	1.586(2)	C(8)–C(9)	1.490(3)
P(3)–N(2)	1.595(2)	O(1)–C(8)	1.413(3)
N(1)–P(1)–N(3)	114.01(9)	Cl(1)–P(2)–Cl(2)	99.67(4)
N(1)–P(2)–N(2)	121.16(10)	Cl(3)–P(3)–O(1)	99.01(6)
N(2)–P(3)–N(3)	117.15(10)	P(1)–C(4)–C(7)	108.54(14)
P(1)–N(1)–P(2)	119.05(11)	C(4)–C(7)–C(8)	134.0(2)
P(2)–N(2)–P(3)	117.24(11)	C(7)–C(8)–O(1)	125.1(2)
P(1)–N(3)–P(3)	113.75(11)	C(8)–O(1)–P(3)	115.63(14)
C(1)–P(1)–C(4)	112.59(10)	O(1)–P(3)–N(3)	99.01(6)
Torsion angles			
N(3)–P(1)–N(1)–P(2)	23.25(15)	N(3)–P(1)–C(4)–C(7)	−68.49(17)
N(1)–P(1)–N(3)–P(3)	−45.44(14)	N(3)–P(3)–O(1)–C(8)	78.04(16)
N(2)–P(2)–N(1)–P(1)	−1.91(16)	O(1)–P(3)–N(3)–P(1)	−79.89(13)
N(1)–P(2)–N(2)–P(3)	2.32(16)	P(3)–O(1)–C(8)–C(7)	−55.4(3)
N(3)–P(3)–N(2)–P(2)	−25.52(15)	P(1)–C(4)–C(7)–C(8)	57.7(3)
N(2)–P(3)–N(3)–P(1)	47.46(14)	C(4)–C(7)–C(8)–O(1)	−5.4(4)
C(4)–P(1)–N(3)–P(3)	74.92(13)		

Table 6 Composition, conversion and molecular weight data for copolymers from compound **5**

	mol % **5**							
Run[a]	Feed	Polymer	*t*/d	Conversion (%)	$10^{-3}\bar{M}_{\mathrm{w,l}}$	$10^{-3}\bar{M}_{\mathrm{n,l}}$	$10^{-3}\bar{M}_{\mathrm{w,v}}$	$10^{-3}\bar{M}_{\mathrm{n,v}}$
1	10	4.5	3	55	70	35	65	40
2[b]	40	13.5	5	17	55	20	55	25
3	61	18	3	1.4	15	10	15	10
4[b]	5	0.3	3 (h)	67	730	370	540	100

[a] Runs 1–3 with styrene and 4 with mma as comonomer. [b] Bimodal molecular weight distribution.

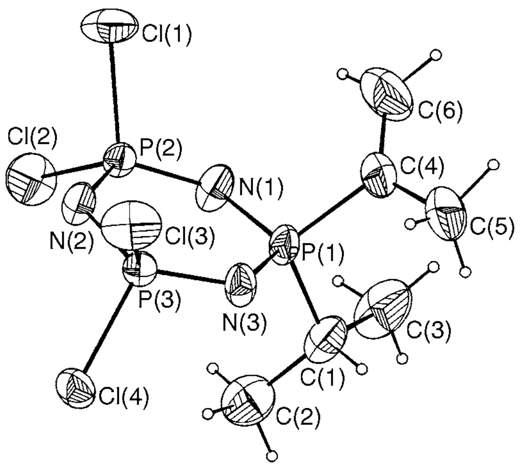


Fig. 3 Perspective ORTEP[30] drawing of the non-hydrogen atoms of compound **5** with the atom labelling scheme for the non-hydrogen atoms. Details as in Fig. 2

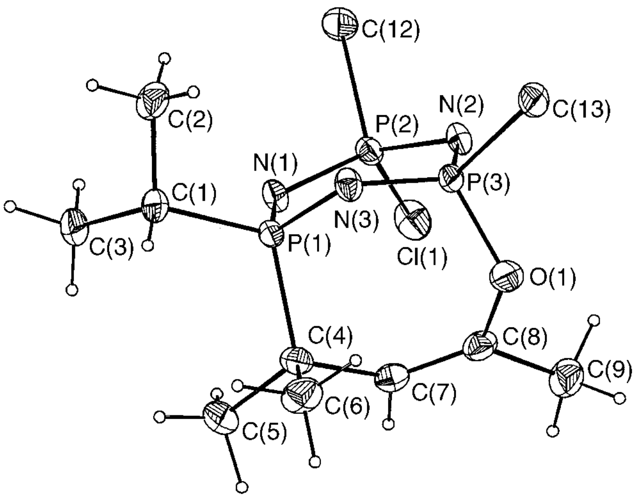
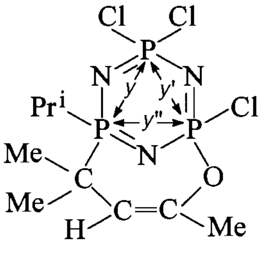


Fig. 4 Perspective ORTEP[30] drawing of the non-hydrogen atoms of compound **6** with the atom labelling scheme for the non-hydrogen atoms. Details as in Fig. 2

and *y*″ is even further reduced to 2.6750(9) Å.[37] In **7** the values of *y*, *y*′ and *y*″ are 2.787, 2.726 and 2.720 Å, respectively. Again as expected the mean non-bonded P···P distances in **8** [*y* = 2.743(2) and *y*″ = 2.748(2) Å] are not different from that of $(NPCl_2)_3$.

Polymerization reactions with compound 5

The results of the free-radical polymerization reactions with the propene derivative **5** are listed in Table 6. Homopolymerization of **5** failed, whereas in a copolymerization reaction with mma only a very small amount of the inorganic component was incorporated. The polymerization behaviours of similar compounds, $N_3P_3F_5(CMe{=}CH_2)$,[2] $N_3P_3F_5(COEt{=}CH_2)$[2] and $N_3P_3Cl_4Pr^i[COC(O)Me{=}CH_2]$,[38] have been described previously. These precursors are also unable to undergo homopolymerization. However, in copolymerization with the less sterically hindered monomer styrene, copolymers are obtained which contain large amounts of the inorganic monomer. Thus the reluctance of the 1,1-disubstituted inorganic monomers to undergo radical homo- and co-polymerization reactions with mma is very probably due to steric hindrance at the reaction



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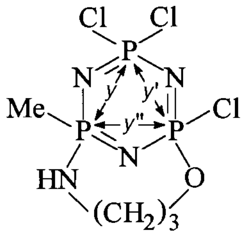

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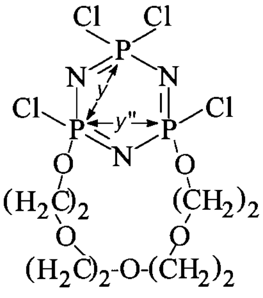

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site. It should be noted that 1,1-disubstituted organic monomers, *e.g.* α-methylstyrene, do not undergo radical addition polymerization due to the low ceiling temperatures of the resulting polymers.

In the copolymerization reaction of compound **5** with styrene 18 mol % of **5** is incorporated at a conversion of only 1.4% (w/w) with 61 mol % of **5** in the feed. Compared with the system $N_3P_3F_5(CMe{=}CH_2)$–styrene it is noted that with the fluoro derivative a maximum incorporation of 37 mol % (with 80 mol % in the feed) can be achieved at a conversion of 37% (w/w).[39] As the polarization of the double bond is almost the same for both **5** and the fluoro derivative (Table 1) the difference in polymerization behaviour between the latter two inorganic monomers must be due to a larger steric hindrance in the case of **5**. This clearly shows that the substituent, *e.g.* the isopropyl group, on the same phosphorus atom as the double bond exerts a large influence on the polymerization behaviour.

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