Controlled Hydrolysis of Hexachlorocyclotriphosphazene and Related, Sulphur-containing Ring Systems

Barteld de Ruiter, Herman Winter, Theo Wilting, and Johan C. van de Grampel *
Department of Inorganic Chemistry, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Reactions of the ring systems $(NPCl_2)_3$, $(NPCl_2)_2NSOX$, and $NPCl_2(NSOX)_2$ (X = Cl or Ph) with water in acetonitrile in the presence of $AsPh_4Cl$ or $KCl–C_{12}H_{24}O_6$ (1,4,7,10,13,16-hexaoxacyclo-octadecane) afford salts derived from hydroxy derivatives of these rings. In all compounds the introduced oxygen ligands are exclusively attached to phosphorus atoms. In addition to monosubstituted derivatives some disubstituted ones can also be isolated. For $(NPCl_2)_3$ a non-geminal structure for the two isomeric disubstituted derivatives was established, whereas the derivative of $(NPCl_2)_2NSOCl$ appears to have a geminal structure. The difference in reaction behaviour of these two ring systems is rationalized in terms of the different base strengths of the rings. The ^{31}P n.m.r. spectra of the salts are briefly discussed.

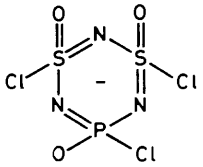
During the past several years the interest in the field of inorganic ring systems such as hexachlorocyclotriphosphazene $(NPCl_2)_3$ has been focused particularly on the development of inorganic polymers with novel properties [1,2] and of oligomeric derivatives that can be used in the development of new drugs.[3-5] For both types of compounds the hydrolytic behaviour is of extreme importance, in particular with respect to their biomedical applications. Although hydrolysis must be an essential type of reaction of $(NPCl_2)_3$, surprisingly little is known of its mechanism. Only fully substituted compounds $N_3P_3R_6$ (R = amino, alkoxy, or aryloxy) have been investigated in detail.[6-9]

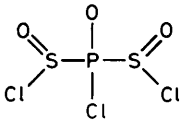
Substitution reactions of chlorophosphazenes with water have seldom been described, although a number of isolated hydroxy-substituted cyclophosphazenes (whether or not rearranged to rings with phosphazane character), prepared in various ways, are known.[10-13] The few reports dealing with the controlled hydrolysis of chlorocyclophosphazenes (leading finally to phosphoric acid and ammonia) [14] point to the instability of the intermediate partially hydrolyzed derivatives.[15] To investigate the nature of these intermediate products we deemed it wise to find a way to avoid the isolation of these poorly characterizable compounds themselves.

In a preliminary communication we have already described the preparation of some salts of a monohydroxy derivative of the ring system *cis*-$NPCl_2(NSOCl)_2$ (including the crystal structure of one of them), which appeared to be stable and well defined crystalline solids.[16] We have now extended these investigations to the ring systems $(NPCl_2)_3$ and $(NPCl_2)_2NSOX$ (X = Cl or Ph). These also reacted with water, affording derivatives that could be isolated as their tetraphenylarsonium or (1,4,7,10,13,16-hexaoxacyclo-octadecane)potassium salts. In addition to the monosubstituted derivatives we also found disubstituted compounds, which are formed *via* geminal as well as non-geminal substitution patterns.

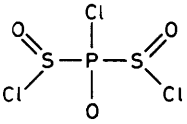
Results and Discussion

Monosubstituted Derivatives of *cis*-$NPCl_2(NSOCl)_2$.—When isomerization experiments with *cis*-$NPCl_2(NSOCl)_2$ using dimethylamine hydrochloride [17] were carried out in acetonitrile that had not been dried thoroughly, we noticed that hydrolysis could be a disturbing side reaction. Attempts to prepare the non-isolable hydrolysis product(s) as their tetramethylammonium or tetraphenylarsonium salt resulted in the isolation of the stable salts of the $[NPClO(NSOCl)_2]^-$ ion (shown below), described in a preliminary report.[16]





(1α, 3α, 5α) (1)



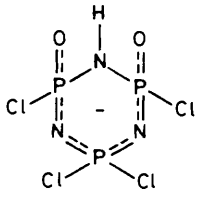
(1α, 3α, 5β) (2)

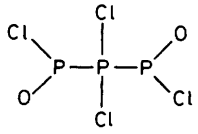
Hydrolytic phenomena were also observed during fluorination reactions with *trans*-$NPCl_2(NSOPh)_2$ and *cis*-$NPCl_2(NSOCl)_2$ using KF in acetonitrile in the presence of the macrocyclic ether 18-crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane, $C_{12}H_{24}O_6$). Whilst reactions under extremely dry conditions readily afforded *trans*-$NPF_2(NSOPh)_2$,[18] no fluorinated derivatives of *cis*-$NPCl_2(NSOCl)_2$ were obtained. However, reaction of *cis*-$NPCl_2(NSOCl)_2$ in wet acetonitrile using KF and 18-crown-6 gave a product which was identified as $[K(C_{12}H_{24}O_6)]^+[NPClO(NSOCl)_2]^-$. Its yield increased by using stoicheiometric quantities of water and crown ether. Reactions with KCl instead of KF afforded the same product, in both cases a mixture of two isomeric forms (1a) and (2a) (ratio 4 : 1). Essentially the same ratio was found for the tetraphenylarsonium salts (1b) and (2b) {throughout this paper $[K(C_{12}H_{24}O_6)]^+$ salts are indicated by compound numbers (*n*a), $[AsPh_4]^+$ salts by (*n*b)}. A crystal structure determination of the most abundant isomer of the analogously prepared $[NMe_4]^+[NPClO(NSOCl)_2]^-$ revealed that its anion possesses the (1α,3α,5α) configuration.[16] In view of the similarity of the i.r. spectra it can be assumed that the anions in (1a) and (1b) also have this configuration. As the configuration around the sulphur centres will almost certainly not have been changed during the reaction, the less abundant isomers (2a) and (2b) contain the (1α,3α,5β)-$[NPClO(NSOCl)_2]^-$ ion.

Reactions with $(NPCl_2)_3$.—The nature of the introduced oxygen ligand in (1) and (2) suggests that similar reactions also apply to other phosphazene systems. Furthermore, a recent description of reactions between $(NPCl_2)_3$ and carboxylic acids shows that salts with the $[(NPCl_2)_2NPClO]^-$ ion are not without precedent.[12]

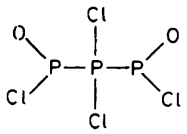
The replacement of NSOCl by less electronegative $NPCl_2$ units lowers the electrophilicity of the phosphorus centre, and, in general, reactions of $(NPCl_2)_3$ with water (molar ratio 1 : 1) in acetonitrile in the presence of $AsPh_4Cl$ or $KCl–C_{12}H_{24}O_6$

required more forcing conditions than corresponding ones with $NPCl_2(NSOCl)_2$. The main products (*ca.* 60% crude yield) were the salts containing the anion $[(NPCl_2)_2NPClO]^-$, (3a) and (3b); (3b) formed well defined (1 : 1) adducts with a number of polar solvents (MeCN, CH_2Cl_2). In addition, *ca.* 25% of $(NPCl_2)_3$ could be recovered, whilst according to the ^{31}P n.m.r. spectrum of the crude product, side products, (4a,b) and (5a,b) [ratio (4) : (5) *ca.* 3 : 1], had been formed in 15% yield. These side products appeared to be the main constituents of the reaction mixtures when an excess of water was used. Elemental and spectral analyses of these mixtures indicated that they were mixtures of isomers, each compound containing the anion $[N_3P_3Cl_4O_2H]^-$ (shown below); this means that two P–Cl bonds had been hydrolyzed. The ^{31}P n.m.r. spectra showed similar patterns for all compounds: a doublet in the δ(PClO) region (~ −4 p.p.m.) and a triplet in





trans (4)



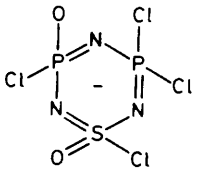
cis (5)

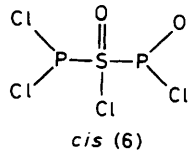
the δ(PCl_2) region (15—20 p.p.m.). The splitting patterns as well as the chemical shifts pointed to the presence of one PCl_2 and two equivalent PClO centres within the anions of each compound. The equivalence of the PClO centres can either be the result of a fast hydrogen-exchange process between P–OH and P–O^- groupings (or a more complicated process also involving ring nitrogen atoms), or of a 'symmetric' location of the hydrogen atom, *i.e.* attached to the ring nitrogen atom between the PClO centres. In this case, the PClO centres are equivalent, as the existence of several resonance hybrids accounts for a symmetric distribution of the negative charge. The latter possibility is the most probable one because of the following arguments. (*a*) From the basicity studies of Shaw [19] it is evident that the nitrogen atom between the PClO centres in the $[NPCl_2(NPClO)_2]^{2-}$ ion will be by far the most basic one of this ring, and hence be the first one to be protonated. (*b*) The ^{31}P n.m.r. spectra showed no significant changes, if recorded at −70 °C (CD_2Cl_2). Exchange processes, if any, would therefore have an extremely low energy of activation. (*c*) I.r. spectra of the mixtures in $CDCl_3$ solution showed a sharp absorption at 3 360 cm^{-1}, which has been ascribed to an N–H stretching mode in similar systems.[20]

In view of the above considerations we propose a structure for the anions of the 'disubstituted' products as shown above. The appearance of two isomers for each salt can now easily be accounted for: $[NPCl_2(NPClO)_2H]^-$ can exist in two forms, *cis* and *trans*. As a substituent-solvating effect [21] can, in principle, be operative in this system, we tentatively ascribe the *trans* structure to the more abundant isomer (4).

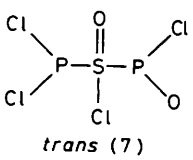
Reactions with $(NPCl_2)_2NSOCl$.—As expected, $(NPCl_2)_2NSOCl$ takes an intermediate position between $(NPCl_2)_3$ and $NPCl_2(NSOCl)_2$ regarding its reactivity towards water. The monosubstituted compounds were always accompanied by a disubstituted one, the components being difficult to separate. Only the $[K(C_{12}H_{24}O_6)]^+$ salt of the monohydroxy derivative, which consisted of two isomers (6a) and (7a) in a ratio of 3 : 1, could be isolated. We assume that in the most abundant isomer (6a) the oxygen atoms in the $[NPCl_2(NPClO)(NSOCl)]^-$ ion (shown below) are *cis* with respect to each other {*cf.* the assignments to the $[NPClO(NSOCl)_2]^-$ salts}.

The disubstituted derivatives (8a,b) were most readily



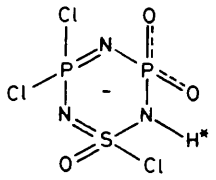


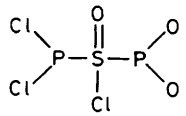
cis (6)



trans (7)

formed, and were the only products if an excess of water had been used in the reactions. Unexpectedly, we never succeeded in detecting more than one isomeric form of both salts. Both the ^{31}P n.m.r. splitting pattern (AX spin system) and the ^{31}P chemical shift values (+19 and −4 p.p.m.) suggested that the structure of (8) was the geminal one. The possibility that one of the substitution steps had taken place at the sulphur centre was rejected, for this would have afforded a mixture of probably three isomeric disubstituted products. An *X*-ray structure determination of (8a) (although the data are of a quite provisional nature) unambiguously showed that its anion indeed possesses the geminal structure $[NPCl_2(NHPO_2)(NSOCl)]^-$ (shown below; * indicates the probable position of H).[22] On the basis of i.r. spectral data (absorption at 3 360 cm^{-1} in $CDCl_3$ solution) we assume the hydrogen atom to be nitrogen-bonded, which is in conformity with the tentative bond lengths.

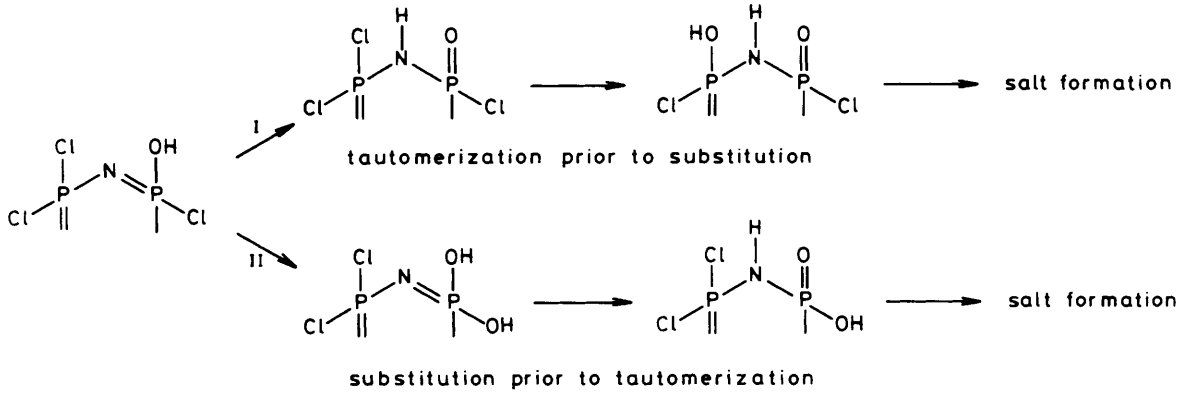




(8)

Mechanism of the Second Substitution Step.—Chlorine substitution reactions at the phosphorus centres of $(NPCl_2)_2NSOCl$ have never shown essential differences from corresponding reactions with $(NPCl_2)_3$.[23] It is shown here, that under certain conditions profound differences can occur, and to explain these, the differences in the electronic structures of the two ring systems must be taken into consideration. Quantum chemical calculations, as well as basicity measurements, have shown that the replacement of a PCl_2 by a SOCl unit in the phosphazene ring affects the charge density at the ring nitrogen atoms; aminolyzed derivatives of $(NPCl_2)_3$ are distinctly more basic than analogous derivatives of $(NPCl_2)_2NSOCl$.[24]

It is our conviction that the different behaviour of the two ring systems is due to this difference in basicity. Thus, the nitrogen atoms of $(NPCl_2)_2NPClOH$ are more readily protonated than those of $NPCl_2(NPClOH)(NSOCl)$, and therefore a phosphazene–phosphazane tautomerization will be more favoured in the former compound. If this tautomerization is faster than the second hydrolysis step, the second molecule of water will preferably attack a PCl_2 centre (in accordance with Allen's theory,[25] as the oxo-ligand can be considered as a π-donor), affording a non-geminal disubstituted compound (route I in Scheme). However, if the second step is faster than the tautomerization, then a mechanism may become operative that is initiated by a proton abstraction (although the liberated HCl will tend to obstruct this), leading to a geminal disubstituted product (route II). We assume that route I applies to $(NPCl_2)_3$, and route II to $(NPCl_2)_2NSOCl$.



Scheme.

Table 1. Phosphorus-31 n.m.r. parameters (in $CDCl_3$)

Anion [a]		δ(PCl_2)/p.p.m.	δ(PClO)/p.p.m.	δ(PO_2)/p.p.m.	^2J(PP)/Hz
(1α,3α,5α)-[NPClO(NSOCl)$_2$]$^-$	(1a)		−11.4		
	(1b)		−12.3		
(1α,3α,5β)-[NPClO(NSOCl)$_2$]$^-$	(2a)		−9.0		
	(2b)		−9.3		
[(NPCl$_2$)$_2$NPClO]$^-$	(3a)	20.7	−0.9		44.6
	(3b)	20.0	−2.6		42.4
trans-[NPCl$_2$(NPClO)$_2$H]$^-$	(4a)	16.0	−4.2		42.0
	(4b)	15.4	−5.1		41.5
cis-[NPCl$_2$(NPClO)$_2$H]$^-$	(5a)	19.3	−3.1		38.8
	(5b)	18.6	−4.2		35.1
cis-[NPCl$_2$(NPClO)(NSOCl)]$^-$	(6a)	23.4	−6.0		66.5
	(6b)	23.0	−6.5		66.7
trans-[NPCl$_2$(NPClO)(NSOCl)]$^-$	(7a)	25.2	−4.4		59.0
[NPCl$_2$(NHPO$_2$)(NSOCl)]$^-$	(8a)	19.2		−3.7	45.9
	(8b)	19.0		−4.6	44.6
(1α,3β,5α)-[NPClO(NSOPh)$_2$]$^-$	(9a)		−3.5		
	(9b)		−7.0 [b]		
[NPCl$_2$(NPClO)(NSOPh)]$^-$ (isomer 1)	(10a)	23.2	−2.8		50.6
[NPCl$_2$(NPClO)(NSOPh)]$^-$ (isomer 2)	(11a)	21.9	−3.0		57.0

[a] Compounds (*n*a) are [K(C$_{12}$H$_{24}$O$_6$)]$^+$ salts, compounds (*n*b) are [AsPh$_4$]$^+$ salts. [b] In CD_3CN.

Reactions with trans-$NPCl_2(NSOPh)_2$ *and* $(NPCl_2)_2NSOPh$.—The phenylated ring systems *trans*-$NPCl_2(NSOPh)_2$ and $(NPCl_2)_2NSOPh$ could be converted into salts of their monosubstituted derivatives by reflux for 20 h. We isolated the two salts of (1α,3β,5α)-[NPClO(NSOPh)$_2$]$^-$ (9a,b), and the [K(C$_{12}$H$_{24}$O$_6$)]$^+$ salt of [NPCl$_2$(NPClO)(NSOPh)]$^-$. The latter salt existed in two isomeric forms, (10a) and (11a), in a ratio of (peculiarly) *ca.* 1 : 1. The isomers were not separated.

Disubstituted derivatives of $(NPCl_2)_2NSOPh$ were, unfortunately, never even detected.

Phosphorus-31 N.M.R. Spectra.—The ^{31}P n.m.r. parameters of the salts are summarized in Table 1. The introduction of a negatively charged oxo-ligand leads to a large upfield shift of the ^{31}P nucleus directly involved, its value varying from 20 p.p.m. [$(NPCl_2)_3$ compared with (3)] up to 40 p.p.m. [*cis*-$NPCl_2(NSOCl)_2$ compared with (1) and (2)]. The chemical shifts of the intact PCl_2 groupings remain relatively unaffected. The values of ^2J(PP) slightly decrease on introduction of O^- ligands; the markedly low value for (8) suggests that the presence of an NPO_2^- ring unit profoundly affects the bonding situation within the ring system.

Experimental

General.—Solvents were purified and dried by conventional methods. The compounds *cis*-$NPCl_2(NSOCl)_2$, $(NPCl_2)_2$-NSOCl, *trans*-$NPCl_2(NSOPh)_2$, and $(NPCl_2)_2NSOPh$ were prepared according to published procedures; [26-28] $(NPCl_2)_3$ was kindly provided by Otsuka Chemical Co. Ltd. (Osaka, Japan) and was used after sublimation. Tetraphenylarsonium chloride hydrate (Merck), 18-crown-6 (Aldrich), and KCl (Merck) were used without purification. The ^{31}P n.m.r. spectra (proton-noise decoupled) were taken with a Nicolet NT 200 instrument, operating at 81.0 MHz, using $(NPCl_2)_3$ (+19.9 p.p.m.) as external standard; the ^2H resonance line of the solvent ($CDCl_3$, CD_3CN) was used for field frequency lock. Chemical shifts are positive in the low-field direction.

Preparations.—All reactions were carried out in acetonitrile, either at room temperature (295 K) or under reflux conditions (355 K). The required amount of water was directly weighed in, or added as a dilute solution in acetonitrile. After the required reaction period (see Table 2) the mixture was filtered, and the volatile part thoroughly removed *in vacuo*. Small amounts of starting materials were removed by consecutive washing of the remaining solid with diethyl ether and ice-cold water. The residue was dried and subsequently purified by recrystallization. This process appeared to be quite critical: the material was dissolved in acetonitrile or dichloromethane, and diethyl ether was added until the solution became opaque. Filtration and cooling of the filtrate gave reasonable results, although substantial loss of material generally could not be avoided (see Table 2). Melting points and analyt-

Table 2. Experimental details of reactions [a]

Ring system [b]	Reagent [b,c] used	Added H_2O (mmol)	Reaction time (h)	Reaction temp. (K)	Main products	Ratio	Solvent of recrystallization	Purified product	Yield (%)
cis-$NPCl_2(NSOCl)_2$	a	40	20	295	(1a), (2a)	4 : 3	CH_2Cl_2–Et_2O (1 : 3)	*d*	78
cis-$NPCl_2(NSOCl)_2$	b	—	2	295	(1b), (2b)	4 : 1	MeCN–Et_2O (1 : 1)	(1b)	72
$(NPCl_2)_3$	a	80	24	295	(3a)		MeCN–Et_2O (1 : 2)	(3a)	18
$(NPCl_2)_3$	b	—	20	355	(3b)		MeCN	(3b)·MeCN [e]	30
$(NPCl_2)_3$	a	40	20	355	(4a), (5a)	4 : 1	CH_2Cl_2–Et_2O (1 : 3)	(4a)	26
$(NPCl_2)_3$	b	12	20	355	(4b), (5b)	5 : 2	MeCN	*d*	30
$(NPCl_2)_2NSOCl$	a	10	20	295	(6a), (7a)	4 : 1	CH_2Cl_2–Et_2O (1 : 3)	(6a)	35
$(NPCl_2)_2NSOCl$	b	—	20	295	(6b), (8b)	1 : 1	n.r.[f]	—	—
$(NPCl_2)_2NSOCl$	a	50	20	295	(8a)		CH_2Cl_2–Et_2O (1 : 3)	(8a)	40
$(NPCl_2)_2NSOCl$	b	—	20	295	(8b)		MeCN–Et_2O (1 : 2)	(8b)	35
trans-$NPCl_2(NSOPh)_2$	a	50	20	355	(9a)		MeCN–Et_2O (1 : 2)	(9a)	22
trans-$NPCl_2(NSOPh)_2$	b	—	20	355	(9b)		MeCN–Et_2O (1 : 1)	(9b)	45
$(NPCl_2)_2NSOPh$	a	10	20	355	(10a), (11a)	1 : 1	MeCN–Et_2O (1 : 2)	*d*	11

[a] In MeCN (100 cm^3). [b] 10 mmol. [c] a = KCl–$C_{12}H_{24}O_6$, b = $AsPh_4Cl·H_2O$. [d] Analytically pure isomeric mixtures. [e] Thorough washing with diethyl ether gave solvent-free (3b). [f] Not recrystallized.

Table 3. Melting points and analytical data

Compound	M.p.[a] (°C)	Analysis [b] (%) C	H	N	S	Cl
(1a), (2a)	—	24.15 (24.20)	4.05 (4.05)	6.90 (7.05)	10.85 (10.80)	18.00 (17.90)
(1b)	157—159 [c]	42.70 (42.70)	3.10 (3.00)	6.30 (6.25)	9.70 (9.50)	15.75 (15.75)
(3a)	144—146	22.90 (22.80)	3.85 (3.85)	6.70 (6.65)		28.20 (28.05)
(3b)	157—160	40.70 (40.50)	2.85 (2.85)	6.10 (5.90)		24.10 (24.90)
(3b)·MeCN	154—156	41.60 (41.50)	3.10 (3.10)	7.55 (7.45)		23.05 (23.55)
(4a)	178—181	23.60 (23.50)	4.25 (4.10)	7.05 (6.85)		22.50 (23.10)
(4b), (5b)	—	41.05 (41 60)	3.05 (3.05)	5.95 (6.05)		21.05 (20.45)
(6a)	166.5—169	23.60 (23.50)	3.90 (3.95)	6.80 (6.85)	5.15 (5.25)	23.30 (23.10)
(8a)	143.5—144.5	24.25 (24.25)	4.25 (4.25)	6.85 (7.05)	5.40 (5.40)	18.05 (17.90)
(8b)	168—171	42.65 (42.70)	3.35 (3.15)	6.25 (6.25)	4.85 (4.75)	15.70 (15.75)
(9a)	133—135	42.55 (42.50)	5.10 (5.05)	6.30 (6.20)	9.25 (9.45)	5.25 (5.25)
(9b)	190—194	56.90 (57.05)	4.05 (4.00)	5.60 (5.55)	8.55 (8.55)	4.65 (4.70)
(10a), (11a)	—	33.20 (33.00)	4.50 (4.45)	6.45 (6.40)	4.90 (4.90)	15.90 (16.25)

[a] Uncorrected. [b] Calculated values in parentheses. [c] With decomposition.

ical data are summarized in Table 3. I.r. spectral data were consistent with the proposed structures.

Acknowledgements

This work was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization of Advancement of Pure Research (Z.W.O.). The ^{31}P n.m.r. spectra were kindly recorded by Dr. A. A. van der Huizen.

References

1 H. R. Allcock, *Chem. Technol.*, 1975, **5**, 552; *Polymer*, 1980, **21**, 673.
2 R. E. Singler, N. S. Schneider, and G. L. Hagnauer, *Polym. Eng. Sci.*, 1975, **15**, 321; G. L. Hagnauer, *J. Macromol. Sci., Chem.*, 1981, **16**, 385.
3 J.-F. Labarre, F. Sournies, S. Cros, G. François, J. C. van de Grampel, and A. A. van der Huizen, *Cancer Lett.*, 1981, **12**, 245.
4 H. R. Allcock, P. E. Austin, and T. X. Neenan, *Macromolecules*, 1982, **15**, 689.
5 A. A. van der Huizen, J. C. van de Grampel, W. Akkerman, P. Lelieveld, A. van der Meer-Kalverkamp, and H. B. Lamberts, *Inorg. Chim. Acta*, 1983, **78**, 239.
6 H. R. Allcock and E. J. Walsh, *J. Am. Chem. Soc.*, 1969, **91**, 3102; 1972, **94**, 119.
7 B. W. Fitzsimmons, C. Hewlett, K. Hills, and R. A. Shaw, *J. Chem. Soc. A*, 1967, 679.
8 R. Vilceanu and P. Schulz, *Phosphorus*, 1976, **6**, 231.
9 H. R. Allcock and T. J. Fuller, *J. Am. Chem. Soc.*, 1981, **103**, 2250; H. R. Allcock, T. J. Fuller, and K. Matsumura, *Inorg. Chem.*, 1982, **21**, 515.
10 S. I. Belykh, S. M. Zhivukhin, V. V. Kireev, and G. S. Kolesnikov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1969, **14**, 668.
11 E. J. Walsh, S. Kaluzene, and T. Jubach, *J. Inorg. Nucl. Chem.*, 1976, **38**, 397.
12 F. DiGregorio, W. Marconi, and L. Caglioti, *J. Org. Chem.*, 1981, **46**, 4569.
13 G. J. Bullen, P. E. Dann, M. L. Evans, M. B. Hursthouse, R. A. Shaw, K. Wait, M. Woods, and H. S. Yu, *Z. Naturforsch., Teil B*, 1976, **31**, 995; K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, T. S. Cameron, C. Chan, R. A. Shaw, and M. Woods, *J. Chem. Soc., Chem. Commun.*, 1980, 231; K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1982, 1549.
14 H. R. Allcock, 'Phosphorus–Nitrogen Compounds,' Academic Press, New York, 1972, ch. 5 and refs. therein.
15 F. H. Pollard, G. Nickless, and R. W. Warrender, *J. Chromatogr.*, 1962, **9**, 485.
16 F. van Bolhuis, B. de Ruiter, and J. C. van de Grampel, *J. Chem. Soc., Chem. Commun.*, 1981, 1065.
17 B. de Ruiter and J. C. van de Grampel, *J. Chem. Soc., Dalton Trans.*, 1982, 1773.
18 H. Winter and J. C. van de Grampel, unpublished work.
19 R. A. Shaw, *Pure Appl. Chem.*, 1980, **52**, 1063.
20 R. Vilceanu and P. Schulz, *Z. Anorg. Allg. Chem.*, 1977, **436**, 283.

21 J. M. E. Goldschmidt and R. Goldstein, *J. Chem. Soc., Dalton Trans.*, 1981, 1283.
22 F. van Bolhuis, personal communication.
23 B. de Ruiter, H. H. Baalmann, and J. C. van de Grampel, *J. Chem. Soc., Dalton Trans.*, 1982, 2337; J. C. van de Grampel, *Rev. Inorg. Chem.*, 1981, **3**, 1.
24 J.-P. Faucher, J. C. van de Grampel, J.-F. Labarre, S. N. Nabi, B. de Ruiter, and R. A. Shaw, *J. Chem. Res.*, 1977, (*S*) 112, (*M*) 1257.
25 C. W. Allen and R. P. Bright, *Inorg. Chem.*, 1983, **22**, 1291.
26 R. Clipsham, R. M. Hart, and M. A. Whitehead, *Inorg. Chem.*, 1969, **8**, 2431.
27 H. H. Baalmann, H. P. Velvis, and J. C. van de Grampel, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 935.
28 J. B. van den Berg, B. de Ruiter, and J. C. van de Grampel, *Z. Naturforsch., Teil B*, 1976, **31**, 1216.

Received 14*th June* 1983; *Paper* 3/1005