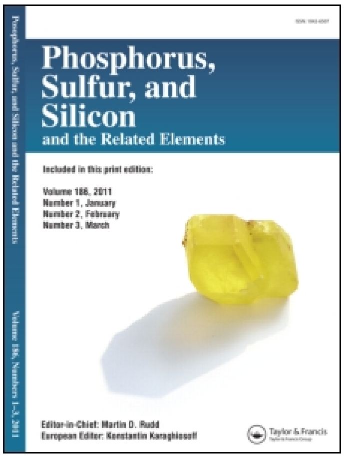

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New Insights into the Chemistry of Cyclic Phosphorus-Nitrogen Compounds

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NEW INSIGHTS INTO THE CHEMISTRY OF CYCLIC PHOSPHORUS-NITROGEN COMPOUNDS

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Abstract High-field two-dimensional ^{31}P NMR spectroscopy (^{31}P-^{31}P COSY) has been used to study the regio- and stereoselectivity in the nucleophilic substitution reactions of the (triphenylphosphazenyl)cyclotriphosphazene, $N_3P_3Cl_5(N{=}PPh_3)$ with trifluoroethoxide or aryloxides and to identify isomeric λ^5-bicyclic phosphazenes. The structures and conformations of λ^3-cyclotriphosphazanes and their reactivity towards transition metal derivatives and oxidation and oxidative addition reactions have been investigated.

Key Words : cyclophosphazenes, cyclophosphazanes, 2D ^{31}P NMR spectra

INTRODUCTION

As a part of our ongoing programme in the chemistry of cyclic P–N compounds,[1] recent results on three aspects of this chemistry are reported in this paper. These are (a) use of high field ^{31}P NMR spectroscopy to study the regio- and stereoselectivity in the reactions of (triphenylphosphazenyl)-λ^5-cyclotriphosphazene $N_3P_3Cl_5(N{=}PPh_3)$, (b) identification of isomeric λ^5-bicyclic phosphazenes derived from (amino)cyclotetraphosphazenes by 2D ^{31}P-^{31}P COSY measurements and (c) synthesis and reactivity of trifluoroethoxy/aryloxy-λ^3-cyclotriphosphazanes.

NUCLEOPHILIC SUBSTITUTION REACTIONS OF $N_3P_3Cl_5(NPPh_3)$

We had earlier shown that the presence of a $N{=}PPh_3$ group on a cyclophosphazene ring exerts a pronounced directing effect on the incoming substituent in the nucleophilic substitution reactions of $N_3P_3Cl_5(NPPh_3)$ (**1**).[2,3] In particular, the methoxylation of **1** gives a nongeminal derivative with the *cis* isomer predominating. In the present work, the reactions of trifluoroethoxide, 4-methylphenoxide and 4-tertbutylphenoxide with $N_3P_3Cl_5(NPPh_3)$ have been investigated and the major products formed have been identified by highfield ^{31}P-^{31}P COSY and J-resolved spectral measurements on the reaction mixtures. A typical 2D-NMR spectrum is shown in Figure 1. The proposed structures are shown in Figure 2.

The mono trifluoroethoxy derivative $N_3P_3Cl_4(NPPh_3)(OR)$ (**2**, R=CH_2CF_3) and the bis-4-*tert*-butylphenoxy derivative $N_3P_3Cl_3(NPPh_3)(OR)_2$ (**3**, R=$C_6H_4CMe_3$-4) have been isolated as crystalline solids and their structures established by single crystal X-ray diffraction (Figure 3). Compound **2** is the only product at the mono stage of chlorine replacement from **1** by $CF_3CH_2O^-$. Compound **3** is the major isomer formed in the 1:2 stoichiometric reaction of **1** with 4-$Bu^tC_6H_4O^-$.

While the regioselectivity in the nucleophilic substitution reactions of halogeno cyclophosphazenes can be satisfactorily explained, the stereoselectivity is far from completely understood.[3]

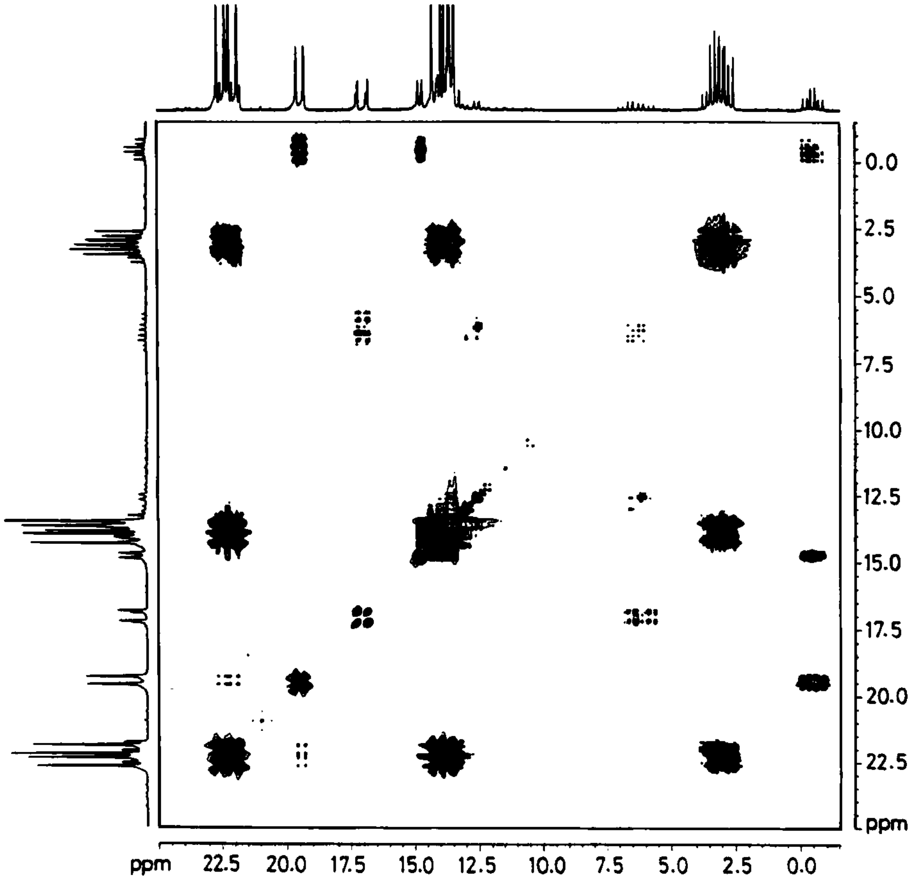


FIGURE 1. The ^{31}P-^{31}P COSY spectrum (162 MHz) of the reaction mixture of **1** with $NaOC_6H_4Bu^t$-4 (1:1) in THF. The major products are **2** and **3**; in addition, unreacted **1** and minor amounts of an isomer of **2** and **3** are also present

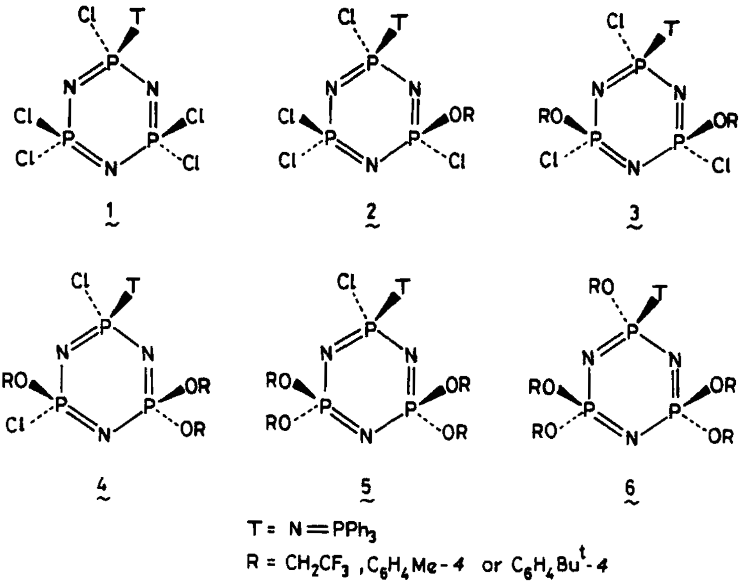


FIGURE 2. Proposed structures for the major products in the reaction of 1 with NaOR

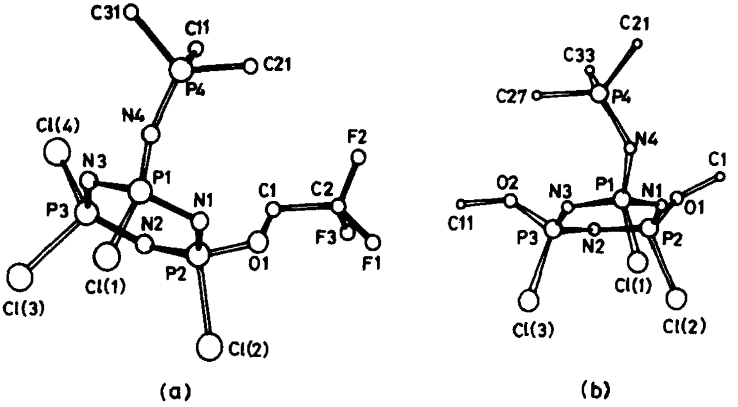
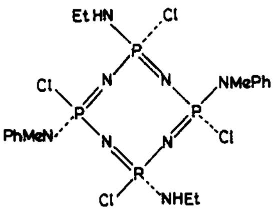


FIGURE 3. Perspective view of molecules (a) **2** (R = CH_2CF_3) and (b) **3** (R = $C_6H_4Bu^t$-4); only *ipso* carbons of the phenyl / aryl rings are shown.

ISOMERIC λ^5-BICYCLIC PHOSPHAZENES

Continuing our interest in the chemistry of λ^5-bicyclic phosphazenes derived from (amino)chlorocyclotetraphosphazenes,[4] we have now been able to show that ^{31}P-^{31}P COSY measurements on the reaction mixtures can yield new insights into the mechanism of this *trans*-annular nucleophilic substitution reaction. We have isolated the nongeminal tetrachloro derivative $N_4P_4Cl_4(NHEt)_2(NMePh)_2$ (**7**) and determined its structure by X-ray crystallography. The reactions of **7** with dimethylamine or ethylamine have been monitored by ^{31}P-^{31}P COSY and J-resolved NMR measurements. The results indicate the formation of bicyclic phosphazenes as well as a cyclotetraphosphazene derivative **8**. More interestingly, when the bis-*t*-butylamino derivative $N_4P_4(NHBu^t)_2Cl_6$ is treated with an excess of ethylamine in the presence of triethylamine in chloroform, ring closure can occur in two ways to give isomeric bicyclic phosphazenes **9a,b**. The formation of these two isomers as well as the fully aminated cyclotetraphosphazene $N_4P_4(NHBu^t)_2(NHEt)_6$ (**10**) has been unambiguously established by ^{31}P-^{31}P COSY measurements at 162 MHz. The assignment of the chemical shifts for the individual isomers is based on the data available on related systems.[6] The spectra of **9a,b** are of the A_2X_2 (δ_A = 11.9, δ_X = 9.8) and A_2XY (δ_A = 13.5, δ_X = 9.1, δ_Y = 8.5) type; that of **10** is of the A_2X_2 (δ_A = 1.4, δ_X = -1.7) type.



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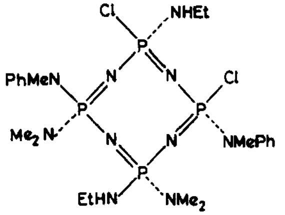

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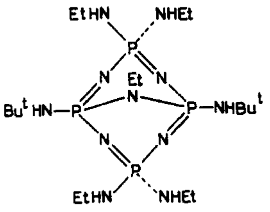
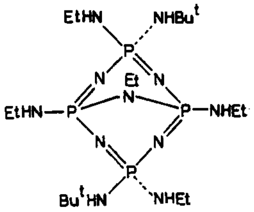
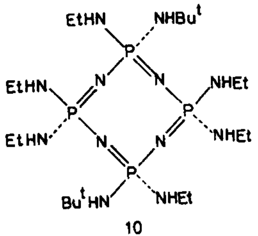


9a



9b

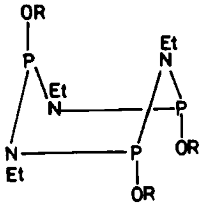


10

λ^3-CYCLOTRIPHOSPHAZANES AND THEIR TRANSITION METAL COMPLEXES

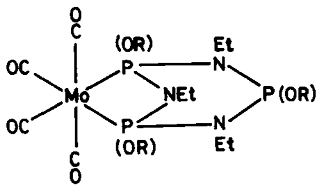
Our recent studies have shown that the P_3N_3 ring in the *cis* and *trans* isomers of $[EtNP\{OC_6H_4Br\text{-}4\}]_3$ exhibits a chair and boat conformation respectively and the 4-bromophenoxy substituents on phosphorus in both the isomers occupy axial positions.[5] In order to study the effect of the presence of a bulky substituent on phosphorus, we have now determined the crystal structure of *trans*-$[EtNP\{OC_6H_3Me_2\text{-}2,6\}]_3$ (**11**). The P_3N_3 ring in **11** adopts a boat conformation and the 2,6-dimethylphenoxy groups occupy the axial positions as in the case of the 4-bromophenoxy derivative. The adoption of such a conformation even with a bulkier substituent on phosphorus supports our earlier bonding model based on 'negative hyperconjugative' interactions between the lone pair on the nitrogen and a P-O σ^* orbital.[1,5]

The reaction of [Mo(CO)$_4$(norbornadiene)] with *cis*-[EtNP(OC$_6$H$_4$Br-4)]$_3$ gives the chelate complex [Mo(CO)$_4${EtNP(OC$_6$H$_4$Br-4)}$_3$] (**12**) as revealed by X-ray crystallography. It is surprising to note that both *cis*-[EtNP(OC$_6$H$_4$Br-4)]$_3$ and *trans*-[EtNP(OC$_6$H$_3$Me$_2$-2,6)]$_3$ yield chelate complexes while *cis*-[EtNP(OCH$_2$CF$_3$)]$_3$ yields a binuclear complex in which two Mo(CO)$_4$ moieties are bridged by two cyclotriphosphazane ligands.[7]



11

R = C$_6$H$_3$Me$_2$-2,6

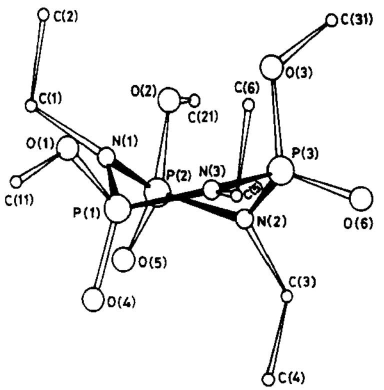


12

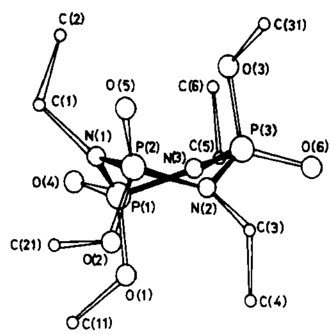
R = C$_6$H$_4$Br-4

OXIDATION AND OXIDATIVE ADDITION REACTIONS OF λ^3-CYCLOTRIPHOSPHAZANES.

Oxidation reactions of *cis*-[EtNP(OCH$_2$CF$_3$)]$_3$ with trimethylamine-N-oxide gives the *cis* isomer of the trioxo λ^5-cyclotriphosphazanes [EtNP(O)(OCH$_2$CF$_3$)]$_3$ (**13a**). The *trans* isomer of [EtNP(O)(OCH$_2$CF$_3$)]$_3$ (**13b**) is obtained by the treament of a *cis-trans* mixture of [EtNP(OCH$_2$CF$_3$)]$_3$ with aqueous H$_2$O$_2$. The two isomers have been characterised by IR and NMR spectroscopy. The solid state structures of both the isomers have been determined by single crystal X-ray diffraction. The six membered P$_3$N$_3$ ring in both isomers exhibit a twist-boat conformation. Perspective views of the core structures of both the molecules are shown below.

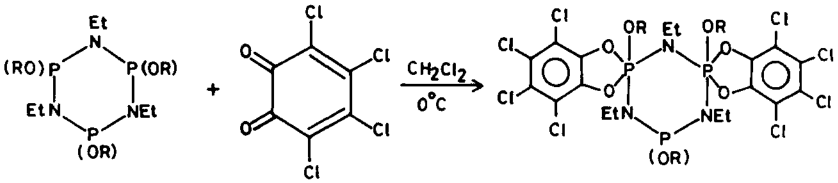


13a



13b

In order to generate P_3N_3 ring systems containing both $\lambda^3\sigma^3$ and $\lambda^5\sigma^5$ phosporus centers, the oxidative addition reactions of λ^3-cyclotriphosphazanes with various diketones have been carried out. The reaction of either *cis* or *trans* isomer of $[EtNP(OR)]_3$ ($R = C_6H_4Br$-4) with tetrachloro-*ortho*-benzoquinone yields $[(EtN)_3\{P(OR)\}\{P(OR)(O_2C_6Cl_4)\}_2]$ (**14**) in which two of the phosphorus atom have undergone oxidative addition. The ^{31}P NMR spectrum of **14** shows an ABX pattern; the AB multiplet is observed for the λ^5-phosphorus centers ($\delta_A = -50.2$, $\delta_B = -51.8$) and the λ^3-phosphorus resonates as a doublet of doublet ($\delta_X = 140$). Further studies on the structure of compounds of this type are in progress.



$R = C_6H_4Br-4$

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