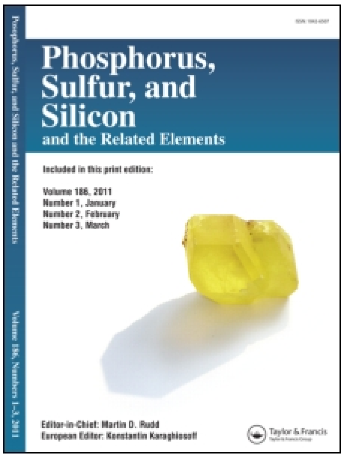

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Cyclotriphosphazanes and Bicyclic Tetraphosphapentazanes

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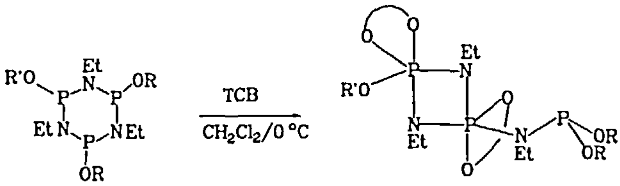
An unusual ring contraction-rearrangement occurs in the reactions of trifluoroethoxy/aryloxy λ^3-cyclotriphosphazanes and the bicyclic phosphazane, $(EtN)_5P_4(OPh)_2$ (L) with tetrachloro-1,2-benzoquinone (TCB) to give λ^5-cyclodiphosphazanes. The bicyclic phosphazane monoxide, $(EtN)_5P_4(O)(OPh)_2$ (L′) undergoes oxidative addition with TCB with retention of the P_4N_5 ring. Treatment of bicyclic phosphazane L and its monoxide L′ with $[Mo(CO)_4(NBD)]$ (NBD = norbornadiene) gives the chelate complexes $[Mo(CO)_4(P\text{-}P)]$ (P-P = L or L′). The structures of the products have been elucidated by high field ^{31}P NMR and X-ray crystallographic studies.

Keywords: cyclotriphosphazanes; bicyclic tetraphosphapentazanes; P-N ring conformation; negative hyperconjugation

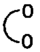
In contrast to the chemistry of λ^3–cyclodiphosphazanes, the chemistry of λ^3–cyclotriphosphazanes and bicyclic tetraphosphapentazanes is less well investigated.[1] In this paper, we report further studies on a novel rearrangement reaction of λ^3–cyclo*tri*phosphazanes with TCB to yield λ^5–cyclo*di*phosphazanes as well as the synthesis and characterisation of bicyclic phosphazanes and their reactivity towards TCB and $[Mo(CO)_4(NBD)]$.

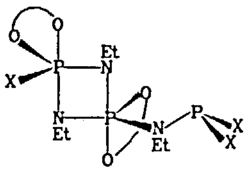
CYCLOTRIPHOSPHAZANES

The λ^3–cyclotriphosphazanes **1a–d** react with TCB to give the λ^5–cyclodiphosphazanes **2a–d** as a result of an unusual ring contraction–rearrangement.[2] The solid state structures of **2a** and **2d** consist of a planar four–membered P_2N_2 ring in which the phosphorus centres are pentacoordinated and one of them bears a $-N(Et)P(OR)_2$ moiety. The aryloxy substituent and aminophosphite moiety are *cis* to one another in **2a** (*gauche* configuration) whereas they are *trans* to each other in **2d** (*trans* configuration). The geometry of the pentacoordinated phosphorus atoms is distorted trigonal bipyramidal. NMR spectroscopic studies indicate that **2a, b** and **d** exist as two isomers in solution. These are assigned *gauche* (A) and *trans* (B) configurations. On the other hand, the ^{31}P–^{31}P COSY NMR spectrum of **2c** shows the presence of four isomers **A–D** shown below of which **A** and **B** are more abundant.

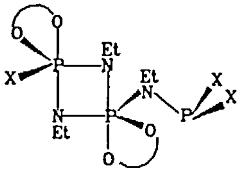


(1a) R = R' = $C_6H_3Me_2$–2,6 (2a)
(1b) = C_6H_4Br–4 (2b)
(1c) = CH_2CF_3 (2c)
(1d) R = $C_6H_3Me_2$–2,6; R' = C_6H_4Br–4 (2d)

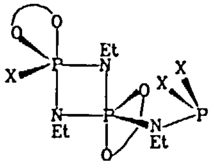
 = $O_2C_6Cl_4$



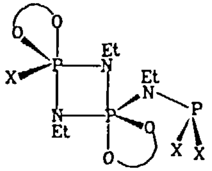
A



B



C

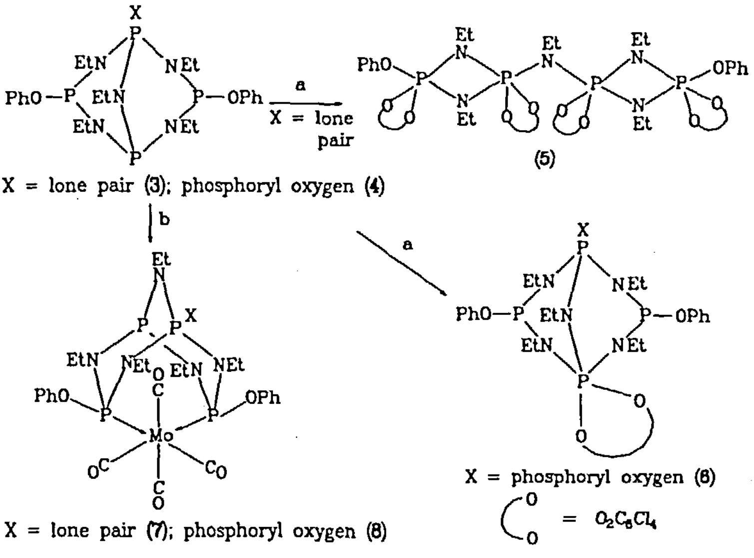


D

(X = OCH_2CF_3)

BICYCLIC TETRAPHOSPHAPENTAZANES

The chlorobicyclic phosphazanes, $(EtN)_5P_4(O)_nCl_2$ (n = 0 or 1) react with NaOPh to give the diphenoxy derivatives **3** and **4** which exist as two isomers in solution as shown by ^{31}P NMR data. Isomers of **3** could not be separated; the major isomer of **4** could be isolated in a pure state by fractional crystallisation from petrol. Oxidative addition of **3** with TCB yields **5** by a double ring contraction–rearrangement. The ^{31}P NMR spectrum of **5** indicates the presence of two isomers. The monoxide **4** undergoes oxidative addition with TCB at the bridging λ^3–phosphorus to give **6** in which the P_4N_5 ring is retained. Reaction of **3** or **4** with $[Mo(CO)_4(NBD)]$ yields the chelate complex **7** or **8** in which the two peripheral phosphorus atoms are coordinated to the metal. The solid state structure of **4** reveals that the two P_3N_3 rings adopt the twist conformation and the phenoxy substituents occupy 'pseudo axial' positions. On the other hand, the two P_3N_3 rings in **6** adopt an irregular and the twist conformations. The P_3N_3 rings in **7** and **8** adopt the chair conformation with the phenoxy substituents occupying 'pseudo equatorial' positions. The structural and conformational changes can be explained by a bonding model based on 'negative hyperconjugation'.[3,4]



X = lone pair (3); phosphoryl oxygen (4)

(5)

X = phosphoryl oxygen (6)

$= O_2C_6Cl_4$

X = lone pair (7); phosphoryl oxygen (8)

a) TCB/C_6H_6/0 °C ; b) [$Mo(CO)_4(NBD)$]/petrol/60 °C

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