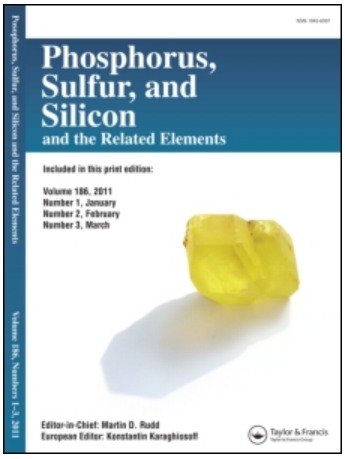

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SKELETAL STABILIZATION: A BASIS FOR NEW CLASSES OF CYCLOPHOSPHAZANES

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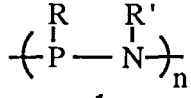
Reactions involving skeletally stabilized intermediate phosphazanes yield new cyclophosphazanes. Thermolysis of $C_6H_4(NH)_2PPh$ (**9**) yields $(PhP)_4$ and the λ^5 phosphazane $[C_6H_4(NH)_2]_2PPh$ (**10**); **10** upon cyclocondensation with $PhPCl_2$ yields *cis,trans-* and *cis,cis-* spiro λ^3-λ^5-λ^3 phosphazanes $[C_6H_4(N)_2PPh]_2PPh$ (**12**). Reaction of the bis(silyl) cyclophosphazane $C_6H_4(NSiMe_3)_2PPh$ with $PhPCl_2$ yields triphosphazane $C_6H_4[NP(Ph)Cl]_2PPh$ (**13**); **13** with 1,2-$(NH_2)_2C_6H_4$ forms cyclotriphosphazane $C_6H_4(N_2PPh)(PPh)_2C_6H_4(NH)_2$ (**14**). **14** is the key intermediate in formation of several new $[(C_6H_4N_2PPh)]_2$-$(PPh)(PR)$ (R = Ph, Me) cleft-containing cyclotetraphosphazanes (**17**). Synthesis and structural characterization of the new phosphazanes are described.

Keywords: phosphazanes; cyclophosphazanes; triphosphazanes, tetraphosphazanes, aminophosphines

INTRODUCTION

Cyclophosphazanes, compounds based on phosphorus-nitrogen single bonds (**1**), in contrast to cyclophosphazenes (**2**), have received relatively little study. Three ring system types, **3** - **5**, have been studied



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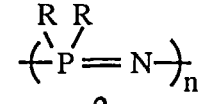

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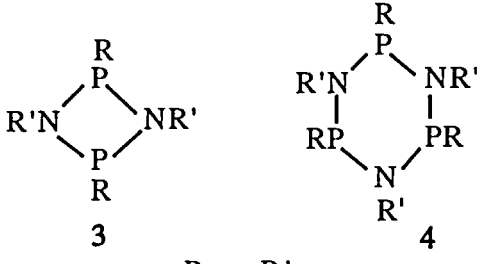
primarily[1-10] and of these only the four-membered ring 1,3,2,4-diazadiphosphetidines (3) have been examined in detail.[1-5] In view



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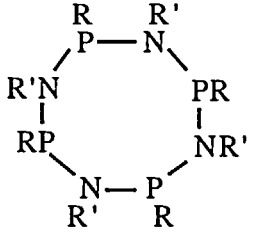
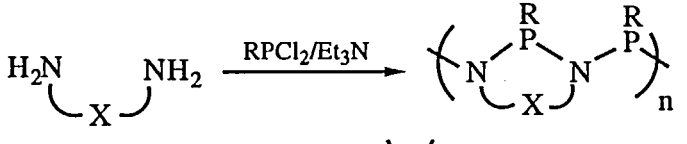


5

of this and in recognition of the potential donor coordination character of cyclophosphazanes,[3,4] we sought routes to new rings that might have both interesting structural and reactivity properties.

In previous work, we showed that by introduction of a bridging group (X) between adjacent nitrogen atoms in a system of alternating phosphorus and nitrogen atoms it is possible to attain degrees of phosphazane chain extension (6) not otherwise accessible (eqn. 1).[11-14]



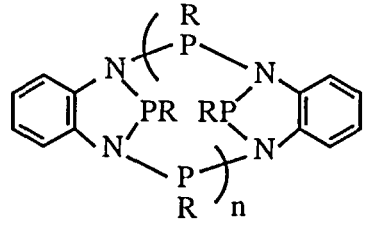
(1)

R = Ph, Me; X = CH_2CH_2, 

6

This technique, referred to as "skeletal stabilization", has allowed synthesis of oligomeric/polymeric phosphazanes and first members of a new crown cyclophosphazane class, 7 and 8.[13,14] Now we describe

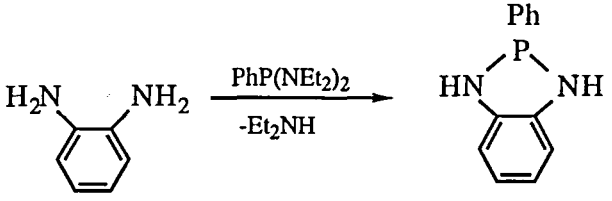
studies in which we extend this skeletal stabilization approach to other cyclophosphazane syntheses.



7, R = Me, Ph, n = 2
8, R = Me, n = 3

DISCUSSION

A key compound in the work described below is the cyclophosphazane **9**, which is best obtained from the transamination of $PhP(NEt_2)_2$ with $1,2\text{-}(NH_2)_2C_6H_4$ (eqn 2).[15] Reaction occurs in toluene at 95 °C. Typically we obtain yields of >90 %. Compound **9**

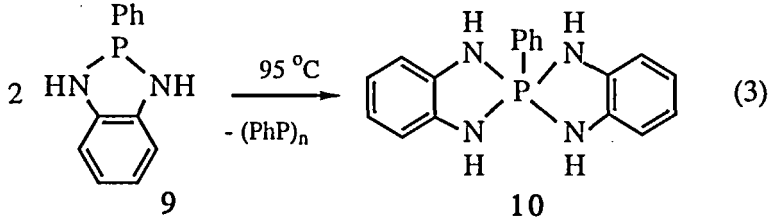


(2)

9

is stable at 25 °C in toluene, but upon solvent removal and thermolysis for 48 hours, disproportionation occurs forming cyclopolyphosphines $(PhP)_{4,5}$ and the novel λ^5-tetraazaphosphane **10** (eqn. 3).

Compound **10** is characterized both by spectral data and single crystal x-ray analysis (see Figure 1). The structure consists of an approximately trigonal bipyramidally arranged group of four NH groups and a phenyl group, with the phenyl group occupying an equatorial



(3)

position. In solution **10** is non-rigid. The ^{31}P NMR spectrum down to - 80 °C shows only the 1:4:6:4:1 pentent (δ -68) expected from a group

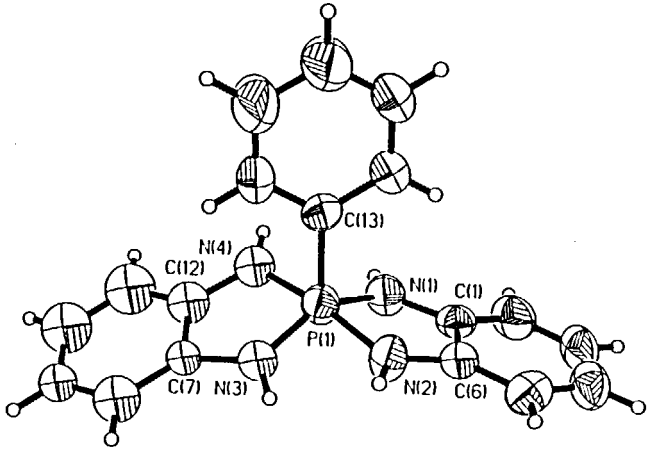
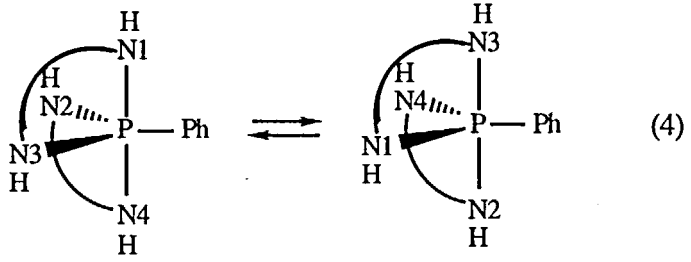


FIGURE 1. Structure and numbering system for **10**.

of four NH based protons exchanging among the equatorial and axial bonding positions (eqn. 4).



(4)

Compound **10** is a rare phosphazane type; it should be noted that thermolysis of non stabilized bis(amino)phosphines does not yield analogous compounds. Although it is reported that thermolysis of $PhP(NHEt)_2$ yields products which could result from disproportionation (eqn. 5),[16] in our hands a reaction proceeds only with

$$2PhP(NHEt)_2 \longrightarrow Ph(EtNH)_2P{=}NEt + Et_2NH + 1/n(PhP)_n \quad (5)$$

great difficulty and only the $(PhP)_{4,5}$ is unambiguously present.

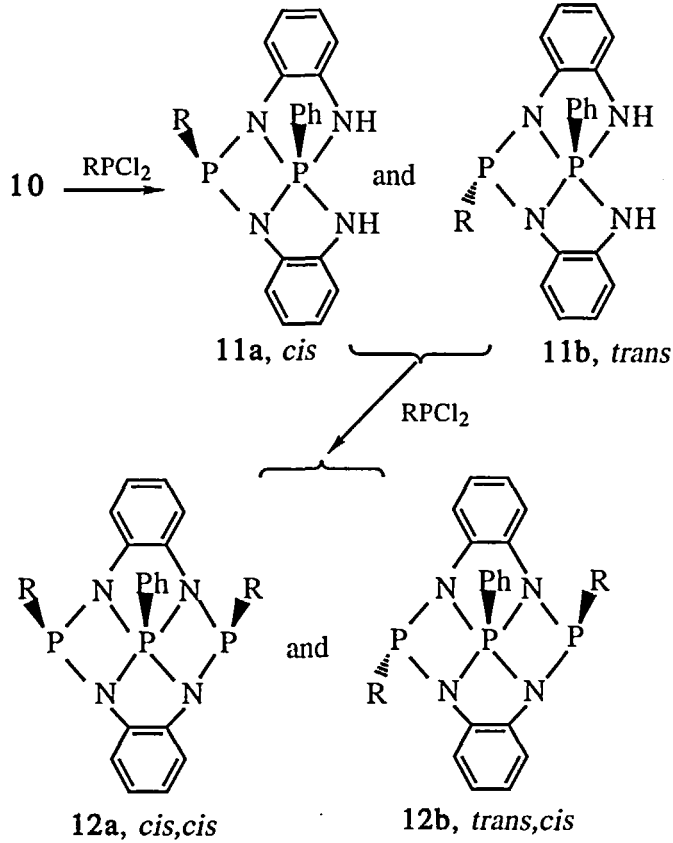


FIGURE 2. Formation of **11a/b** followed by **12a/b.**

Tetraphosphazane **10** is a valuable intermediate for synthesis of other classes of new ring compounds. Reaction of **10** with $PhPCl_2$ and Et_3N leads to cyclocondensation and formation of λ^3-λ^5 *cis-* and *trans-* diphosphazanes, **11a** and **11b**, followed by the *cis,cis-* and *cis,trans-* λ^3-λ^5-λ^3 spiro triphosphazanes, **12a** and **12b** (see Figure 2). Interestingly, no *trans,trans-* form of **12** is observed, either because it rapidly rearranges to the *cis,trans-* isomer or for steric reasons it is unable to form from **11b** in the final condensation step. Compound **12b** undergoes ready isomerization to the more stable **12a**;[17] both can be characterized by spectral data and as their λ^4-λ^5-λ^4 disulfide derivatives by x-ray crystallography. The structure of the *cis.cis-* disulfide of **12a** is shown in Figure 3.

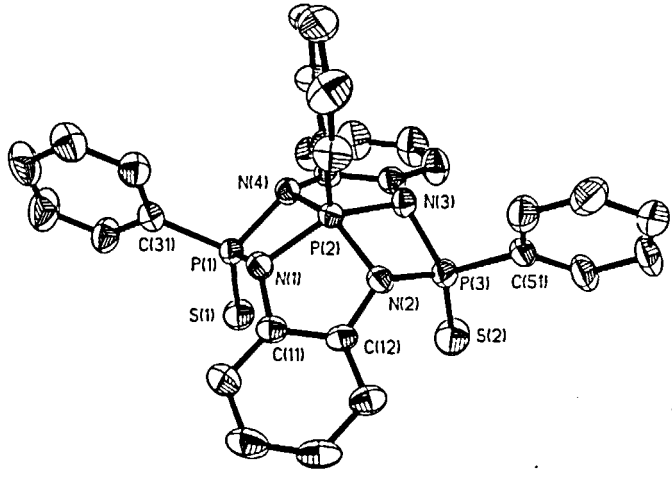
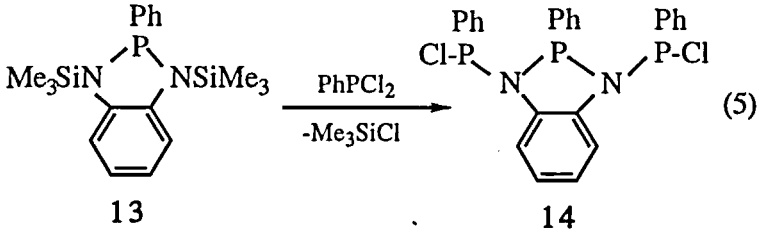


FIGURE 3. Structure of the disulfide of **12a**.

A bis(silyl) derivative of **9**, compound **13**, is a key intermediate for formation of cyclotriphosphazanes, cyclotetraphosphazanes and their derivatives. The **13**, obtained in high yield from $PhPCl_2$ reaction with 1,2-$(Me_3SiNH)_2C_6H_4$, reacts with additional $PhPCl_2$ forming the acyclic triphosphazane **14** (eqn. 5). It, in toluene, exists as the expected

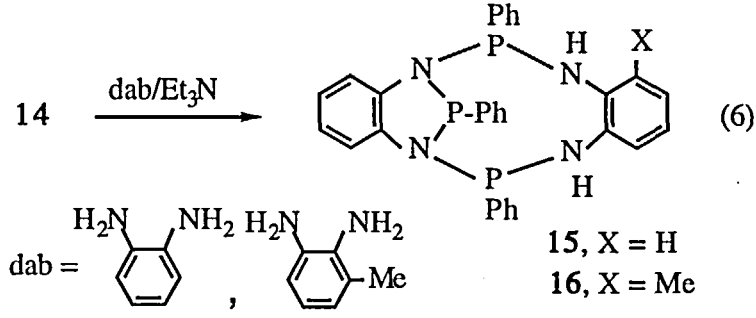
three diastereomers. However, in acetonitrile ^{31}P NMR spectral analyses show only one isomer, likely the result of configurational equilibration through P-Cl bond ionization.

Reaction of **14** with 1,2-diaminobenzenes leads to new



13 14 (5)

cyclotriphosphazanes, e.g. **15** and **16**. Note that **16** is a chiral product.



(6)

Spectral properties of **15** and **16** are as expected; x-ray analysis (see Figure 4) confirms the structure as a 10-membered ring with a PhP group bridging one pair of adjacent nitrogen atoms. Like the previously reported tetraphosphazanes **7** and **8**,[13,14] the triphosphazanes contain a molecular cleft between the upward pointing phenyl rings on P(2) and P(3) into which novel substrate coordination might be expected.[14]

An especially valuable feature of **15/16** cyclotriphosphazanes is that they can be used as intermediates for synthesis of a variety of "cleft-containing" tetraphosphazanes. For example, reactions of $RPCl_2$ (R =

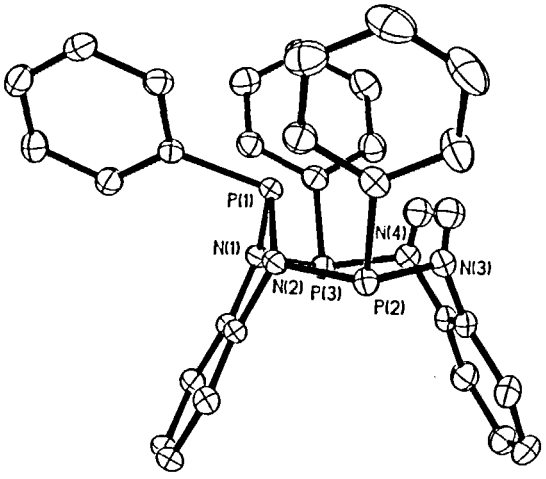
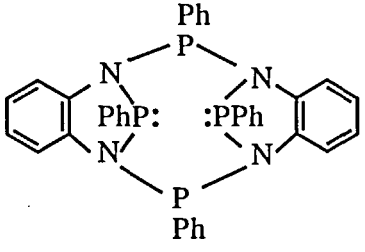


FIGURE 4. Structure of **15**.

Me, Ph) with **15** and Et_3N yield known **7** and the new unsymmetrical **17** in nearly quantitative reactions.



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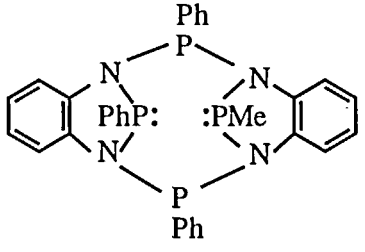

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Further studies of the new cyclophosphazanes **10** - **12** and **15** - **17** are in progress and will be reported later.

Acknowledgments

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