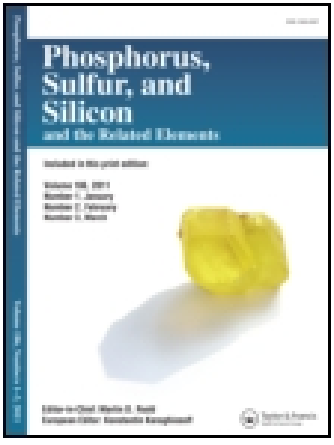

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Skeletal Stabilization: A Basis for New Classes of Cyclophosphazanes

Robert M. Hands , Monte Helm , Bruce Noll & Arlan D. Norman

[a] Department of Chemistry and Biochemistry , University of Colorado , Boulder, CO 80309, USA

[b] Department of Chemistry and Biochemistry , University of Colorado , Boulder, CO 80309, USA

[c] Department of Chemistry and Biochemistry , University of Colorado , Boulder, CO 80309, USA

[d] Department of Chemistry and Biochemistry , University of Colorado , Boulder, CO 80309, USA

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SKELETAL STABILIZATION: A BASIS FOR NEW CLASSES OF CYCLOPHOSPHAZANES

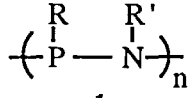
ROBERT M. HANDS, MONTE HELM, BRUCE NOLL AND ARLAN D. NORMAN, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309 USA

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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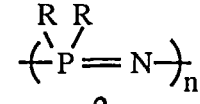

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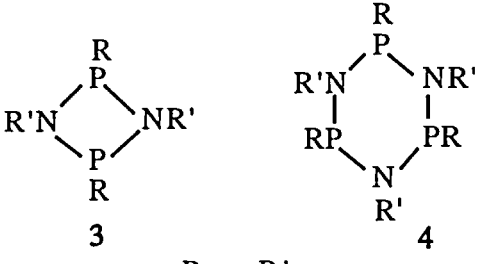
primarily[1-10] and of these only the four-membered ring 1,3,2,4-diazadiphosphetidines (3) have been examined in detail.[1-5] In view



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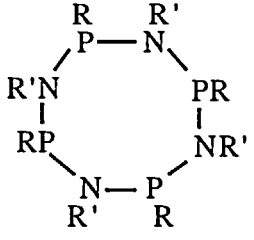
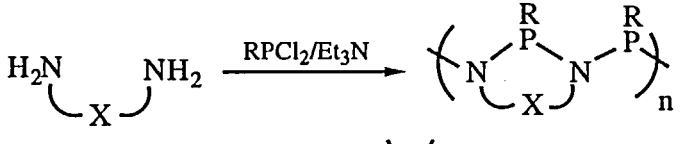


5

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]



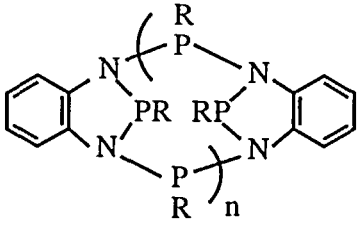
(1)

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

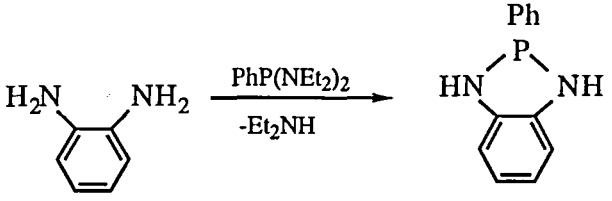
studies in which we extend this skeletal stabilization approach to other cyclophosphazane syntheses.



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**

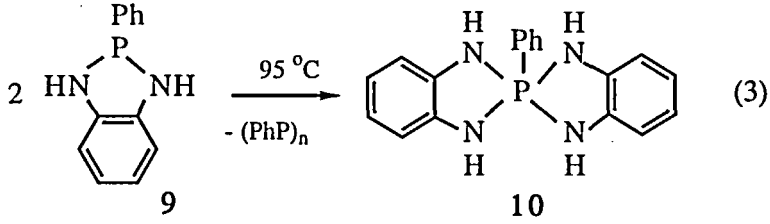


(2)

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

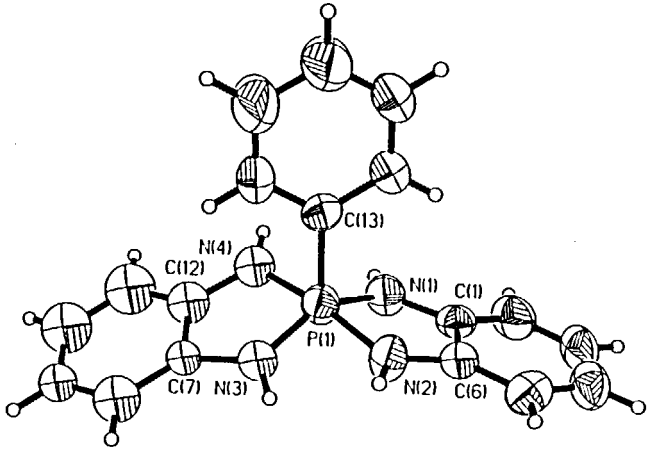
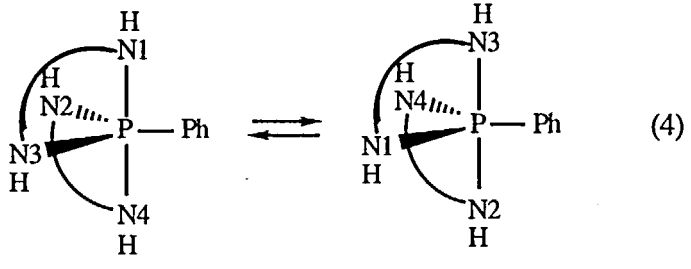


FIGURE 1. Structure and numbering system for **10**.

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.

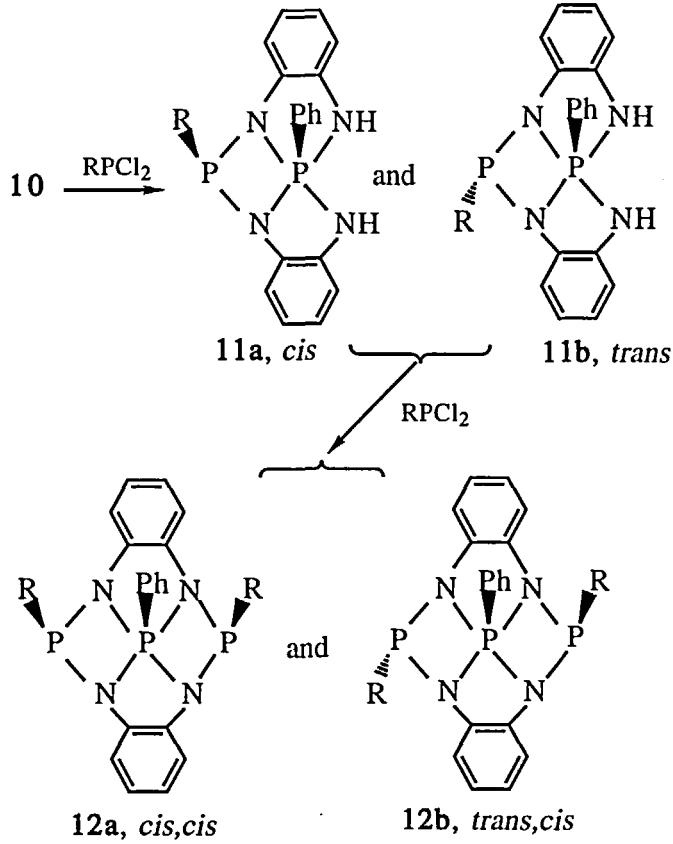


FIGURE 2. Formation of **11a/b** followed by **12a/b**.

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.

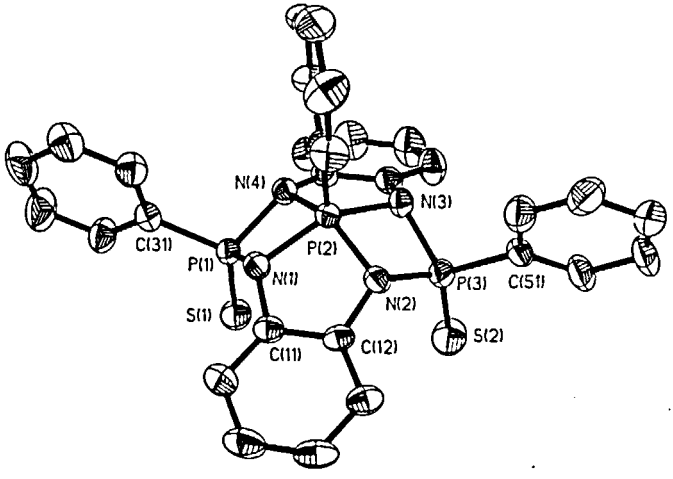
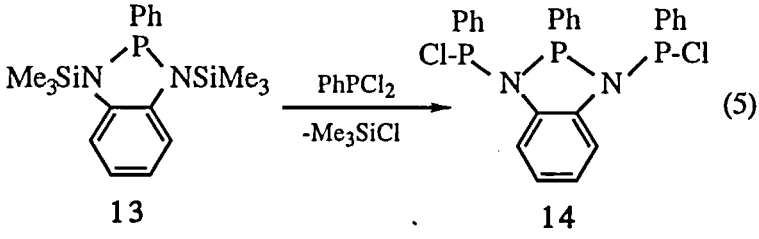


FIGURE 3. Structure of the disulfide of **12a**.

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

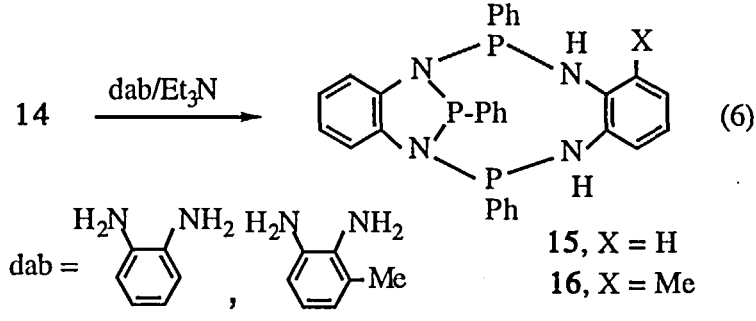
three diastereomers. However, in acetonitrile ^{31}P NMR spectral analyses show only one isomer, likely the result of configurational equilibration through P-Cl bond ionization.

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



(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 =

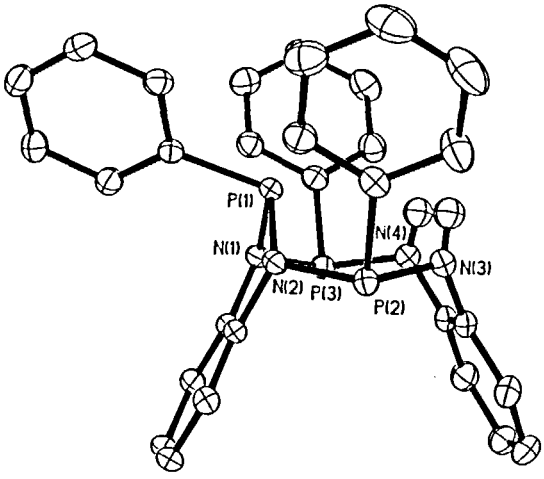
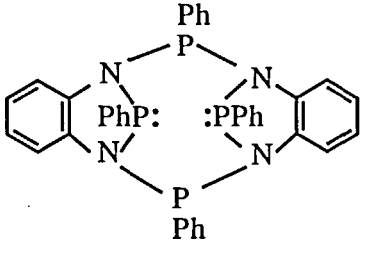


FIGURE 4. Structure of **15**.

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



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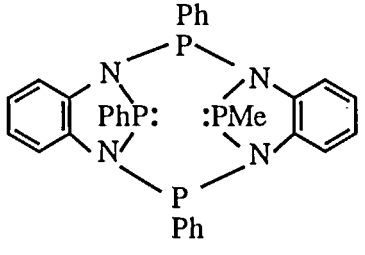

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Further studies of the new cyclophosphazanes **10** - **12** and **15** - **17** are in progress and will be reported later.

Acknowledgments

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