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PHOSPHORUS-BORON AND PHOSPHORUS-SILICON RING SYSTEMS FUNCTIONALIZATION OF PHOSPHORUS RING SYSTEMS

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Abstract The diphosphide $K_2[(t\text{-Bu})\text{P-BN}(i\text{-Pr})_2\text{-P}(t\text{-Bu})]$ reacts with $t\text{-BuPCl}_2$ to form the P_3B ring system $(i\text{-Pr})_2\text{NB}(t\text{-BuP})_3$ **1**. The five-membered P_4B ring system $(i\text{-Pr})_2\text{NB}(t\text{-BuP})_4$ **2** is formed from $K_2[(t\text{-BuP})_4]$ **3** and $(i\text{-Pr})_2\text{NBCl}_2$ analogous to the above reaction.

The reaction of **3** with SiCl_4 or Si_2Cl_6 produces the novel five-membered ring systems $(t\text{-BuP})_4\text{SiCl}_2$ **4** or $(t\text{-BuP})_4\text{Si}(\text{Cl})\text{SiCl}_3$ **5** respectively.

New routes to the synthesis of the monofunctionalized cyclophosphanes $(t\text{-BuP})_2\text{PCl}$ **6** and $(t\text{-BuP})_3\text{PCl}$ **7** and to the new bifunctionalized cyclophosphane $1\text{-Br-3-}[(t\text{-Bu})(\text{Br})\text{P}]\text{-2.4-}(t\text{-Bu})_2\text{-P}_4$ **8** will be reported.

1, **2**, **4**, and **7** could be characterized by X-ray structure analysis; the structures of **5** and **8** could be inferred from NMR data. The ^{31}P NMR spectra of **2** and **7** indicate ($^{10,11}\text{B}$) and ($^{35,37}\text{Cl}$) isotopic shifts respectively.

INTRODUCTION

Until recently, very few phosphorus boron ring compounds with P-P bonds were known, but a number of binary compounds have now been isolated where the basic unit appears to be a P_2 , P_3 , and P_4 fragment in the ring ¹⁻⁶. We have found that **1** and **2** are obtained by cyclocondensation reactions of the type $[1 + 3]$ or $[1 + 4]$ where '1' is a boron dihalide compound.

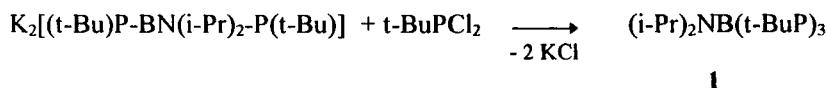
The reaction of **3** with functionalized silicon compounds provides a synthetic pathway to $P_4\text{Si}$ ring systems.

Functionalized cyclophosphanes were obtained by two different routes. Firstly, $[2 + 1]$ cyclocondensation reactions also take place when '1' is a dihalogenoamino phosphane thus leading to monoamino cyclotriphosphane. The amino group can readily be substituted by a chlorine atom when reacted with HCl. This variation circumvents the

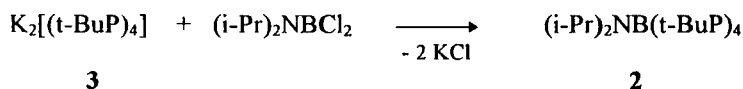
need for reactive silyl or stannyl substituted intermediates⁷. Secondly, in-situ generation of [PX] (X = Cl, Br) from the system PX_3/SnX_2 ⁸ in the presence of $(t\text{-BuP})_3$ results in a ring expansion reaction thus forming a four-membered monohalogenated cyclotetra-phosphane $(t\text{-BuP})_3PX$. Depending on the reaction conditions a second phosphinidene [PX] is added exocyclic to a phosphorus atom of $(t\text{-BuP})_3PX$ in β -position to PX simultaneously followed of a migration of that β -t-Bu group to the PX part.

RESULTS AND DISCUSSION

The new ring systems P_3B triphosphaboretane and P_4B tetraphosphaborolidine resulted from studies aimed at the generation of binary boron-phosphorus rings with P-P bonds. A [3 + 1] cyclocondensation of $K_2[(t\text{-Bu})P\text{-BN}(i\text{-Pr})_2\text{-P}(t\text{-Bu})]$ with $t\text{-BuPCl}_2$ give rise to produce the four-membered P_3B ring¹

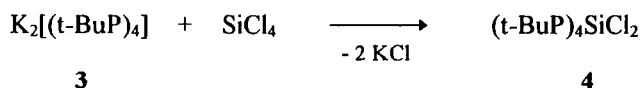


Using this route the [4 + 1] cyclocondensation of $K_2[(t\text{-BuP})_4]$ with $(i\text{-Pr})_2\text{NBCl}_2$ yielded the five-membered P_4B ring system¹.

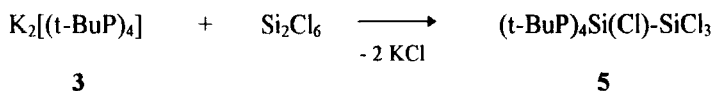


The molecular structure of **1** and **2** was determined from a single-crystal X-ray diffraction study, figure 1 and 2.

The method described above can also be used for the synthesis of phosphorus-silicon rings. The five-membered P_4Si ring was synthesized from **3** and SiCl_4 .

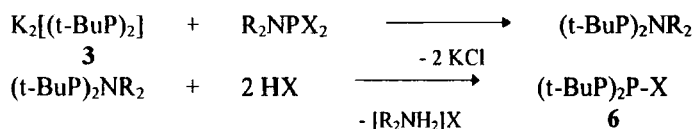


Surprisingly, the two chlorine atoms of the SiCl_2 group do not react with **3** to form the expected spiro compound; this kinetic inertness is due to the steric hindrance by the two t-Bu groups. A X-ray crystal structure analysis of **4** is shown in figure 3. The P_4Si ring system is even formed when **3** is reacted with Si_2Cl_6 .

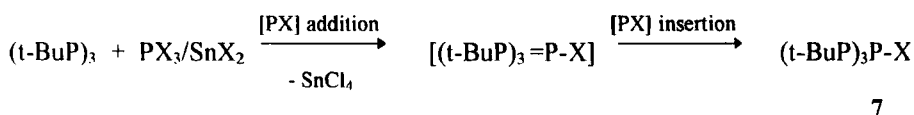


When irradiating **5** with u.v. light, compound **4** and $(\text{SiCl}_2)_n$ are produced and no disilene. The structure of **5** was proved by ^{31}P NMR and MS data; the ^{31}P NMR spectrum shows an AMRX spin system.

We are particularly interested in the synthesis of functionalized cyclophosphanes. We have begun to explore the reactions of $\text{K}_2[(\text{t-BuP})_2]$ with dihalogenoaminophosphanes in order to prepare new types of monofunctionalized cyclotriphosphanes. The replacement of the amino group by halogen atoms can easily be achieved with HX ($\text{X} = \text{Cl}, \text{Br}$).

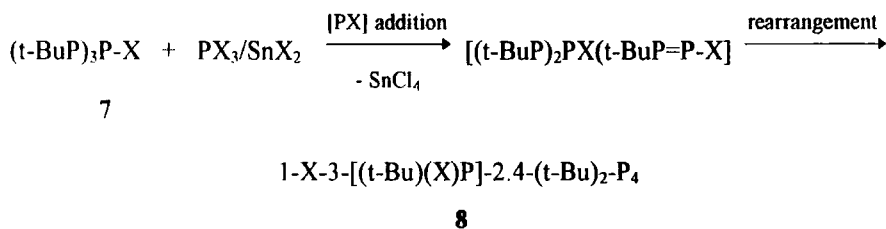


Furthermore, functionalization of cyclotetraphosphane was achieved by insertion of in-situ generated phosphinidene $[\text{PX}]$ into the P_3 skeleton of cyclotriphosphane.



The multiplets of the ^{31}P NMR spectrum of **7** show satellites which are attributed to the $^{35,37}\text{Cl}$ isotopomers. **7** was characterized by a X-ray structure analysis, Figure 4.

Depending on the reaction conditions $[\text{PX}]$ can even add to **7**, leading to an intermediate, which rearranges by migration of an α -t-Bu group to the exocyclic $(=\text{PX})$ group thus forming a bifunctionalized phosphino halogeno cyclotetraphosphane.



The ^{31}P NMR spectrum of **8** corresponds to a ABMRX spin system.

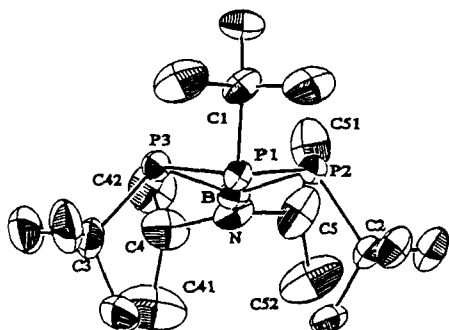


FIGURE 1 The Molecular Structure of $(i\text{-Pr})_2\text{NB}(\text{t-BuP})_3$ 1

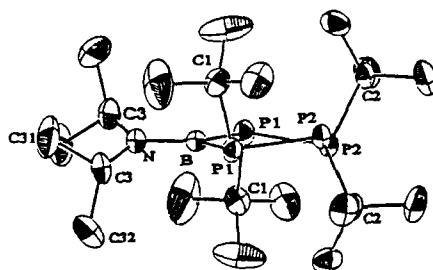


FIGURE 2 The Molecular Structure of $(i\text{-Pr})_2\text{NB}(\text{t-BuP})_4$ 2

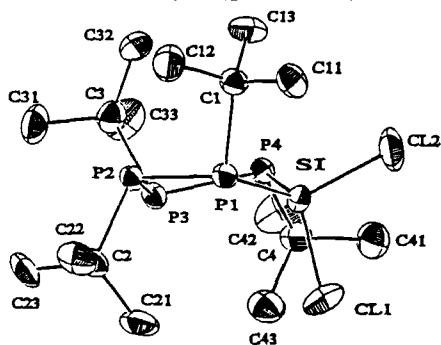


FIGURE 3 The Molecular Structure of $(\text{t-BuP})_4\text{SiCl}_2$ 4

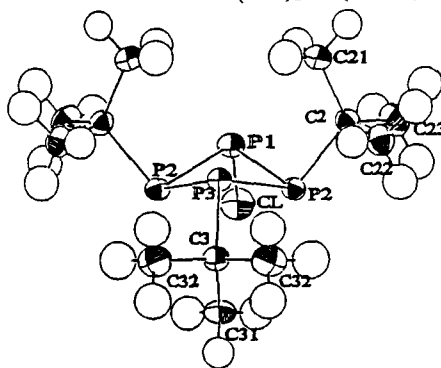


FIGURE 4 The Molecular Structure of $(\text{t-BuP})_3\text{PCl}$ 7

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