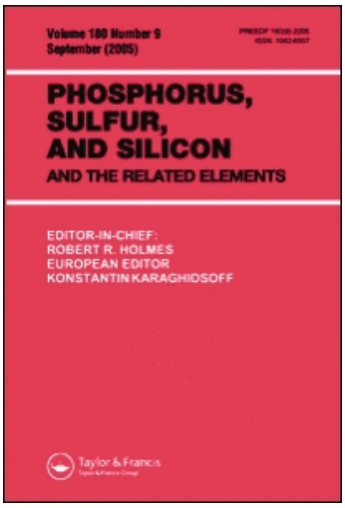

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PHOSPHORUS-BORON AND PHOSPHORUS-SILICON RING SYSTEMS FUNCTIONALIZATION OF PHOSPHORUS RING SYSTEMS

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Abstract The diphosphide $K_2[(t\text{-Bu})P\text{-}BN(i\text{-Pr})_2\text{-}P(t\text{-Bu})]$ reacts with $t\text{-BuPCl}_2$ to form the P_3B ring system $(i\text{-Pr})_2NB(t\text{-BuP})_3$ **1**. The five-membered P_4B ring system $(i\text{-Pr})_2NB(t\text{-BuP})_4$ **2** is formed from $K_2[(t\text{-BuP})_4]$ **3** and $(i\text{-Pr})_2NBCl_2$ analogous to the above reaction.
The reaction of **3** with $SiCl_4$ or Si_2Cl_6 produces the novel five-membered ring systems $(t\text{-BuP})_4SiCl_2$ **4** or $(t\text{-BuP})_4Si(Cl)SiCl_3$ **5** respectively.
New routes to the synthesis of the monofunctionalized cyclophosphanes $(t\text{-BuP})_2PCl$ **6** and $(t\text{-BuP})_3PCl$ **7** and to the new bifunctionalized cyclophosphane 1-Br-3-[(t-Bu)(Br)P]-2.4-$(t\text{-Bu})_2$-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 ($^{10,11}B$) and ($^{35,37}Cl$) 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_4Si 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 intermediates [7]. 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 cyclotetraphosphane $(t\text{-BuP})_3PX$. 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 ring [1]

$$K_2[(t\text{-Bu})P\text{-}BN(i\text{-Pr})_2\text{-}P(t\text{-Bu})] + t\text{-BuPCl}_2 \xrightarrow[-\,2\ KCl]{} (i\text{-Pr})_2NB(t\text{-BuP})_3$$

1

Using this route the [4 + 1] cyclocondensation of $K_2[(t\text{-BuP})_4]$ with $(i\text{-Pr})_2NBCl_2$ yielded the five-membered P_4B ring system [1].

$$K_2[(t\text{-BuP})_4] + (i\text{-Pr})_2NBCl_2 \xrightarrow[-\,2\ KCl]{} (i\text{-Pr})_2NB(t\text{-BuP})_4$$

3 **2**

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 $SiCl_4$.

$$K_2[(t\text{-BuP})_4] + SiCl_4 \xrightarrow[-\,2\ KCl]{} (t\text{-BuP})_4SiCl_2$$

3 **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.

$$K_2[(t\text{-BuP})_4] \quad + \quad Si_2Cl_6 \xrightarrow[-\ 2\ KCl]{} \quad (t\text{-BuP})_4Si(Cl)\text{-}SiCl_3$$

3 **5**

When irradiating **5** with u.v. light, compound **4** and $(SiCl_2)_n$ 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 $K_2[(t\text{-BuP})_2]$ 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 (X = Cl, Br).

$$K_2[(t\text{-BuP})_2] \quad + \quad R_2NPX_2 \xrightarrow[-\ 2\ KCl]{} (t\text{-BuP})_2NR_2$$

3

$$(t\text{-BuP})_2NR_2 \quad + \quad 2\ HX \xrightarrow[-\ [R_2NH_2]X]{} (t\text{-BuP})_2P\text{-}X$$

6

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

$$(t\text{-BuP})_3 \ + \ PX_3/SnX_2 \xrightarrow[-\ SnCl_4]{[PX]\ addition} [(t\text{-BuP})_3{=}P\text{-}X] \xrightarrow{[PX]\ insertion} (t\text{-BuP})_3P\text{-}X$$

7

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

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

$$(t\text{-BuP})_3P\text{-}X \ + \ PX_3/SnX_2 \xrightarrow[-\ SnCl_4]{[PX]\ addition} [(t\text{-BuP})_2PX(t\text{-BuP}{=}P\text{-}X] \xrightarrow{rearrangement}$$

7

1-X-3-[(t-Bu)(X)P]-2.4-(t-Bu)$_2$-P_4

8

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

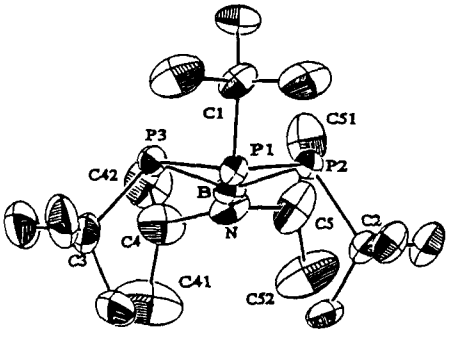

FIGURE 1 The Molecular Structure of $(i\text{-Pr})_2NB(t\text{-BuP})_3$ **1**

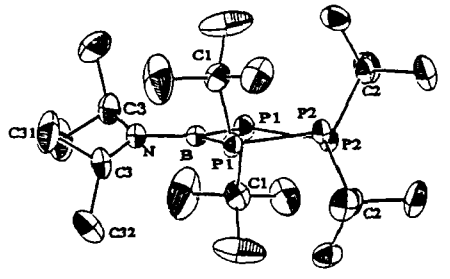

FIGURE 2 The Molecular Structure of $(i\text{-Pr})_2NB(t\text{-BuP})_4$ **2**

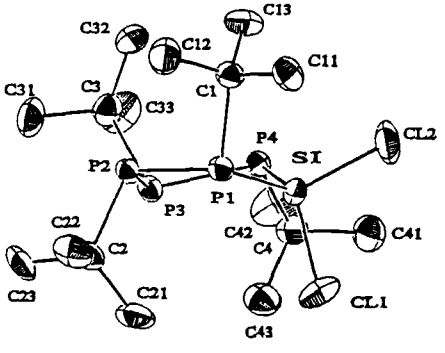

FIGURE 3 The Molecular Structure of $(t\text{-BuP})_4SiCl_2$ **4**

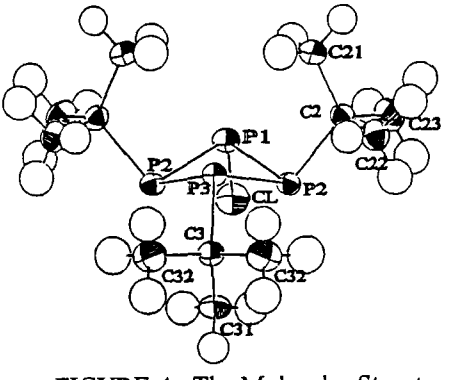

FIGURE 4 The Molecular Structure of $(t\text{-BuP})_3PCl$ **7**

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