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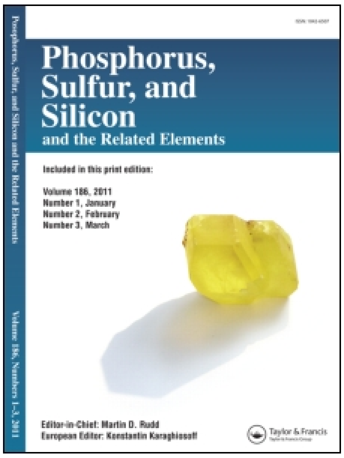

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and Reactions of P-Rich Silylphosphanes

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SYNTHESIS AND REACTIONS OF P-RICH SILYLPHOSPHANES

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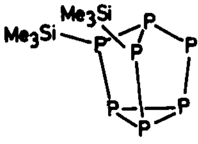
The formation of P-rich compounds like $(Me_3Si)_3P_7$ 1 and $P_4(SiMe_2)_3$ 2 generated from Na/K-alloy, white phosphorus, Me_3SiCl and Me_2SiCl_2, resp., or the formation of 1 from P_4, lithiumalkyles and Me_3SiCl on the other hand occurs in several reaction steps[1].



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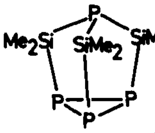

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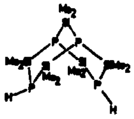
Finally 1 is formed by reaction of Li_3P_7 with Me_3SiCl. Aside of this Li_3P_7 can also be obtained through reactions following the lithiation of silylated diphosphanes and other P-richer derivates[1]. Investigating these reactions seems to be as rewarding as it is difficult to achieve. This is the topic of the presented results of our investigations. It will be reported about: 1. reactions of Li_3P, Li_2PH, $LiPH_2\cdot THF$ with R_2SiCl_2 (R = Me, t-Bu). 2. synthesis of partly silylated, functional (Cl, H, Li, $SiMe_3$) partly alkylated tri- and tetra- as well as cyclotetra phosphanes and their reactions with LiBu. 3. reactions of the P_7-skeleton.

1. The formation of the compounds 1 and 2 from Na/K, P_4 includes the reactions of the generated phosphides with Me_3SiCl and Me_2SiCl_2, resp.. Some more information was expected from the reactions of Li_3P, Li_2PH and $LiPH_2$ with dichlorosilanes. But there are difficulties concerning the isolation of Li_3P and Li_2PH from solutions. Therefore already other authors have tried to produce Li_3P in good solvating ethers by reactions of PH_3 with LiBu[2]. The reaction with Me_2SiCl_2 leads to a mixture of the following compounds.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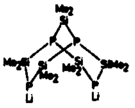

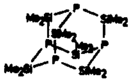
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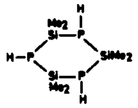
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3 is the precursor of the adamantane-skeleton 4. 3 is formed in the PH- as well as in the lithiated form, which reacts with dimethyldichlorosilane to compound 4. The reactions run in a similar way with Li_2PH. The reaction of $LiPH_2 \cdot THF$ with Me_2SiCl_2 mainly leads to compound 4, too. The reactions of the lithiumphosphides become more easy to survey if they are carried out with $(t\text{-}Bu)_2SiCl_2$, e.g. with $LiPH_2 \cdot THF$.

$$4LiPH_2 + 2(t\text{-}Bu)_2SiCl_2 \longrightarrow HP[Si(t\text{-}Bu)_2]_2PH + 2PH_3 + 4LiCl$$

The appearance of PH_3 characterizes the cross-metallation. The used phosphides still contain P-H-groups. Their P-Lithiation, the reaction with Me_2SiCl_2 as well as the sterical conditions determine the course of the reaction [3].

2. Our further interest in Li-phosphides concerning the formation of the P_7-skeleton is based on the knowledge that $LiP\ P(SiMe_3)_{2\ 2}$ undergoes consecutive reactions when solved in ethers (THF), which lead to Li_3P_7 and some P-richer phosphides by splitting of $(Me_3Si)_3P$ and $LiP(SiMe_3)_2$ [1]. When lithiating persilylated di- or triphosphanes the consecutive reactions are proceeding rather fast. The starting compounds do not contain easily discernable groups which could allow easy identification of the reaction products. Since the cleavage of P-CMe_3 bonds in these reactions is not observed, the investigations of certain steps of these reactions should be simplified by using compounds containing CMe_3 groups. Until now there has been no easy method of synthesis reported for this kind of functional tri- and tetraphosphanes. Silylphosphanes are well known to react with element-halides by splitting off Me_3SiCl and cleavage of the Si-P bond transferring the phosphane

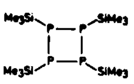
group. This fact enables the formation of functional diphosphanes by reactions of PCl_3 with disilylated phosphanes. These functional diphosphanes react with $LiP(SiMe_3)R$ to tri-phosphanes according to:

$$PCl_3 + RP(SiMe_3)_2 \longrightarrow R(Me_3Si)P\text{-}PCl_2 + Me_3SiCl \qquad (R = CMe_3,\ Me)$$

$$R(Me_3Si)P\text{-}PCl_2 + LiP(SiMe_3)R' \longrightarrow R(Me_3Si)P\text{-}P(Cl)\text{-}P(SiMe_3)R'$$

$$(R' = SiMe_3,\ CMe_3,\ Me)$$

One CMe_3-group in silylated diphosphanes is enough to form a stable phosphide $(Me_3C)(Me_3Si)P\text{-}P(SiMe_3Li$ 7. This fact enables the synthesis of tetraphosphanes by the reaction with $BrCH_2\text{-}CH_2Br$. The influence of CMe_3-groups in a silylated triphosphane will be explained using $[(Me_3C)(Me_3Si)P]_2PLi$ 8 as an example. The primal product of the reactions of 8 (THF) are found to be $LiP(SiMe_3)_2$ and $(Me_3C)P(SiMe_3)_2$. After 60 days one can find the cyclic phosphides $LiP_5(CMe_3)_4$, $LiP_3(CMe_3)_2$, $LiP_4(CMe_3)_3$ and $Li(Me_3Si)P\text{-}P(CMe_3)(SiMe_3)$. Some further information is given by the reactions of the cyclotetraphosphanes 9 to 13 with Li-alkyles.



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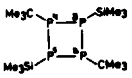

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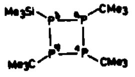

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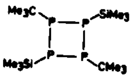

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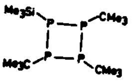

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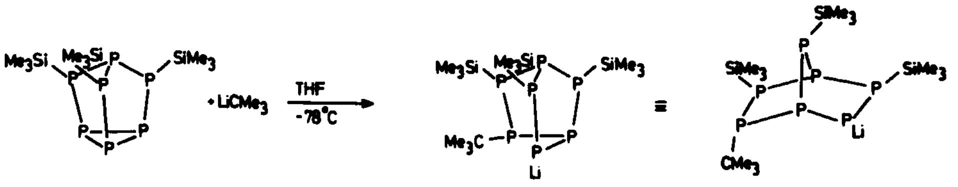
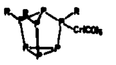
In the first step 12 and 13 react with LiMe and Li(n-Bu), resp. to $LiP_4(CMe_3)_3$ and $LiP_4(CMe_3)_2(SiMe_3)$, resp.. The reactions of 9 starts with the formation of $Li(P\text{-}SiMe_3)_4R$. In the long run $(Me_3Si)_3P$, $LiP(SiMe_3)_2$ and Li_3P_7 have been detected. The P^4-atom in 10 is nucleophilicly attacked by LiR. The reaction in THF leads almost quantitatively to the secondary tetraphosphide $(Me_3Si)_2P^1\text{-}P^2(CMe_3)\text{-}P^3(Li)\text{-}P^4(SiMe_3)R$ and finally results in the formation of $(Me_3Si)_3P$, $LiP(SiMe_3)_2$, Li_3P_7, $Li_2P_7(CMe_3)$. In 11 the nucleophilic attack occurs solely at one silylated P-atom: The primary phosphide isomerises quickly to the secondary, which subsequently leads to the formation of $LiP_5(CMe_3)_4$, $LiP_3(CMe_3)_2$, $P_4(CMe_3)_4$, $LiP(SiMe_3)_2$, $(n\text{-}Bu)P(SiMe_3)_2$. The obtained results give a basic understanding of the above featured consecutive reactions. The loss of $(Me_3Si)_3P$, $(Me_3C)P(SiMe_3)_2$, $LiP(SiMe_3)$ leads to the formation of unstable linear tetra-, penta- and hexaphosphanes, which again after losing higher silylated compounds form cyclic derivatives.

3. Our interest is also directed to the various possible reactions of the P_7-system and especially to the easily surveyable ring-opening reaction of $(Me_3Si)_3P_7$. This can be achieved by the reaction with Li(t-Bu) at -78°C.



Our work on the P_7-skeleton also includes investigations concerning the transition metal-complexes thereof. In contrast to 1 we were successful in the synthesis and identification of the compounds 14 to 18 derived from either Et_3P_7 or $(i\text{-}Prop)_3P_7$.



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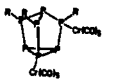

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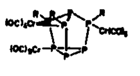

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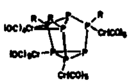

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