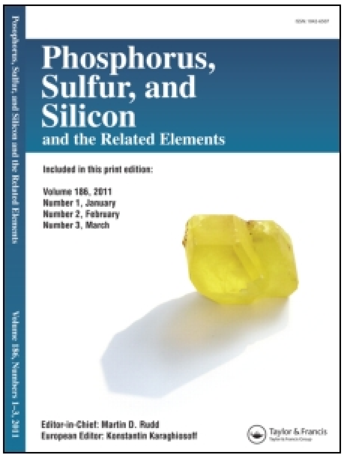

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Formation and chemical behaviour of silylated phosphanes

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FORMATION AND CHEMICAL BEHAVIOUR OF SILYLATED PHOSPHANES

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Our investigations to be presented here have their origin in a number of former results: The formation of $[(Me_3Si)_2P]_2SiMe_2$ [1] and its rearrangement to $P_4(SiMe_2)_6$ (a molecule with adamantane structure) and $P(SiMe_3)_3$, the formation of $P_7(SiMe_3)_3$ and of some cyclic phosphanes by the thermally induced rearrangement of $[(Me_3Si)_2P]_2SiMe_2$ [3], and the formation of $P_7(SiMe_3)_3$ by reacting P_4 with Na/K-alloy and Me_3SiCl. After finding $LiP(SiMe_3)_2$ to be such a versatile reagent we turned to elucidate synthesis and chemical behaviour of $LiP[P(SiMe_3)_2]_2$. This compound is accessible according to the following equation:

$$[(Me_3Si)_2P]_2PH + Li\text{-}t\text{-}Bu \xrightarrow{n\text{-pentane}} LiP[P(SiMe_3)_2]_2 + t\text{-}BuH$$

The phosphide may be isolated from n-pentane as an amorphous yellow powder. The reactions of $LiP[P(SiMe_3)_2]_2$ with PCl_3 are of special interest. Two examples are given below:

$$LiP[P(SiMe_3)_2]_2 + PCl_3 \longrightarrow [(Me_3Si)_2P]_2P\text{-}PCl_2 + LiCl$$

$$[(Me_3Si)_2P]_2P\text{-}PCl_2 \longrightarrow P_3(Cl)[P(SiMe_3)_2](SiMe_3) + Me_3SiCl$$

The latter silylchlorophosphane as other compounds of this type slowly decomposes at 20°C. The examples illustrate that $LiP[P(SiMe_3)_2]_2$ is also a very useful and versatile compound for further syntheses. The lithiation of $[(Me_3Si)_2P]_2PH$ as well as the reactions of $LiP[P(SiMe_3)_2]_2$ with chlorophosphanes only in non-polar solvents take the described way. Ethers cause a sequence of rearrangements which starts with the appearance of orange-red solutions and results eventually in the formation of Li_3P_7.

$$[(Me_3Si)_2P]_2PLi \longrightarrow (Me_3Si)_2P\text{-}P(SiMe_3)\text{-}P(Li)SiMe_3 \longrightarrow$$

$$(Me_3Si)_2P\text{-}P(Li)SiMe_3,\ LiP(SiMe_3)_2,\ P(SiMe_3)_3 \text{ and unknown compounds } \longrightarrow$$

$$Li_3P_7,\ LiP(SiMe_3)_2,\ P(SiMe_3)_3$$

This reaction course (monitored by ^{31}P-nmr spectra) is not restricted to this example. Lithiation of the silylated diphosphanes $(Me_3Si)_2P\text{-}P(SiMe_3)_2$ and $(Me_3Si)_2P\text{-}P(H)SiMe_3$ also starts with the formation of $(Me_3Si)_2P\text{-}P(Li)SiMe_3$. This first reaction step is followed again by a series of rearrangement reactions yielding Li_3P_7, $P(SiMe_3)_3$ and $LiP(SiMe_3)_2$. These characteristic properties of metallated trimethylsilylphosphanes obviously play an important role in the reactions of withe phosphorus. As early as in 1975 we reported the isolation of $P_7(SiMe_3)_3$ as the first molecular compound of the P_7-system, from the reaction of white phosphorus with Na/K-alloy and Me_3SiCl, which was obtained besides some other silylphosphanes $P_{14}(SiMe_3)_4$, e.g. These observations suggest the intermediate formation of M_3P_7 (M = Na, K) and gave rise to investigate the reactions of white phosphorus with Li-alkyls in more detail. We found white phosphorus with LiMe (molar ratio P_4:LiMe = 1:1) in DME or THF at first yield higher molecular lowsoluble lithiumphosphides and on further addition of LiMe also Li_3P_7, Li_2P_7Me and LiP_7Me_2. These react on with Me_3SiCl or MeBr to form $P_7(SiMe_3)_3$, $P_7(SiMe_3)_2Me$, $P_7(SiMe_3)Me_2$ and P_7Me_3, respectively. By higher amounts of LiMe (molar ratio P_4:LiMe □ 1:2) Li_2P_7Me and LiP_7Me_2 are decomposed. The analogous reaction of P_4 with $LiCMe_3$ (molar ratio P_4:$LiCMe_3$ = 1:1) yields Li_3P_7, $Li_2P_7(CMe_3)$, $LiP_7(CMe_3)_2$, and additionally $LiP_4(CMe_3)_3$ and $LiP_3(CMe_3)_2$. Again lowsoluble lithiumpolyphosphides were observed as intermediates. Addition of Me_3SiCl to the reaction mixture affords $P_7(SiMe_3)_3$, $P_7(SiMe_3)_2(CMe_3)$, $P_7(SiMe_3)(CMe_3)_2$, $P_4(SiMe_3)(CMe_3)_3$ and $P_3(SiMe_3)(CMe_3)_2$. In n-hexane/THF the reaction of P_4 with $LiCMe_3$ in the molar ratio of 1:2 predominantly yields the four-membered ring $LiP_4(CMe_3)_3$ besides some of the three-membered ring $LiP(CMe_3)_2$, which with Me_3SiCl yields $P_4(SiMe_3)(CMe_3)_3$ and $P_3(SiMe_3)(CMe_3)_2$.

Obviously in the course of the overall reaction the first isolable intermediates are certain, lowsoluble phosphides, which react on with the lithination reagent to form the mentioned final products. Elucidation of these phosphides and their reactivity is crucial for the understanding of the total reaction course. Their composition was found to be Li_2P_{16}, Li_2P_{14} and "LiP_{13}", depending on the ratio of white phosphorus to lithination reagent. The following equations describe the consecutive steps of the above mentioned reactions proved by starting each of the steps new with the isolated intermediates.

$$P_4 + LiP(SiMe_3)_2 \xrightarrow[THF]{1:0,25} LiP_{13} \cdot 4THF \xrightarrow{LiMe} Li_2P_7Me,\ Li_2P_{16}, PMe_3, P_2Me_4$$

$$P_4 + LiP(SiMe_3)_2 \xrightarrow[THF]{1:0,5} Li_2P_{16} \cdot 7THF \xrightarrow{LiP(SiMe_3)_2} Li_3P_7,\ Li_2P_7(SiMe_3)$$

$$P_4 + LiP(SiMe_3)_2 \xrightarrow{1:1} Li_2P_{14} \xrightarrow{LiMe} Li_3P_7 + Li_2P_7Me$$

$$P_4 + LiP(SiMe_3)_2 \xrightarrow{1:2} Li_3P_7,\ P(SiMe_3)_3$$

Considering these results it is quite clear, that there is a great number of consecutive and competitive reaction steps with formation and decomposition depending on the ratio of concentrations. However, the very first reaction steps affording the complex phosphides are still unknown. Therefore we are especially interested in reactions yielding the P_7-system, but without involving those unelucidated primary steps, occuring in the cleavage of white phosphorus. To get a first view into the complex course of these reactions, the final steps of which probabely coincide with those of the rearrangements mentioned above, metallation of the following cyclotetraphosphanes was also investigated, $P_4(CMe_3)_3(SiMe_3)$, trans-$P_4(CMe_3)_2(SiMe_3)_2$, $P_4(SiMe_3)_4$. One aim was to establish the influence of the degree of silylation, on the reaction course and such on the formation of Li_3P_7. The reaction of the monosilylated four-membered ring with Li-n-Bu in THF yields the $LiP_4(CMe_3)_3$, which is stable in solution. The completely silylated ring yields Li_3P_7, $Li_2P_7(SiMe_3)$, $P(SiMe_3)_3$ and $LiP(SiMe_3)_2$. The composition of the product mixture resulting from trans-$P_4(SiMe_3)_2(CMe_3)_2$ depends on the amount of Li-n-Bu. A molar ratio of 1:2 affords the cyclic compounds $P_4(SiMe_3)(CMe_3)_3$, $LiP_4(CMe_3)_3$ and $LiP_3(CMe_3)_2$ besides some variously substituted derivatives of $P(SiMe_3)_3$. Obviously already the presence of two CMe_3 substituents prevents rearrangement of $LiP_4(SiMe_3)(CMe_3)_2$ to Li_3P_7.

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