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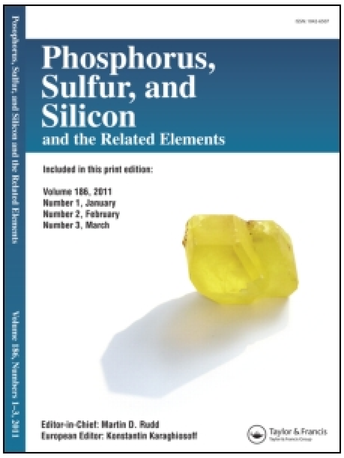

Phosphorus, Sulfur, and Silicon and the Related Elements

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P-Rich Silylphosphanes; Synthesis and Reactions

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P-RICH SILYLPHOSPHANES; SYNTHESIS AND REACTIONS

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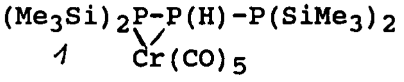
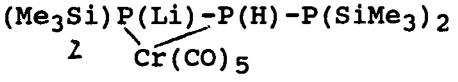
The availability of the phosphanortricyclenes $P_7(SiMe_3)_3$, $P_4(SiMe_2)_3$ [1], P_7R_3 (R = alkyl), their complexchemical properties [2], the formation of Li_3P_7 and other Li-phosphides by the lithiation of $(Me_3Si)_2P-P(SiMe_3)_2$ in ether solution [3] are the causes for the increased interest in P-rich silylphosphanes and lead to the development of new methods for the synthesis of P- functional tri- and tetraphosphanes [4], in which certain P-atoms bear reactive groups ($SiMe_3$,H,Li), while others are blocked by alkyl-groups. Since the formation of transition-metal-complexes reflects, aside of sterical factors, the electronic system of the ligand, it appears to be important, in order to understand the chemistry of P-rich silylphosphanes, to examine their complexing properties. That's why different aspects of the chemistry of P-rich, silylated compounds are surveyed simultaneously.
For a long time the formation of any complex of $P_7(SiMe_3)_3$ with $Cr(CO)_5THF$, that occurs rather easily when P_7Et_3 (initially at an equatorial P-atom) is used instead, could not be observed. Both sterical and electronical reasons have been reported to cause this, particularly since the complexing of $P_4(SiMe_2)_3$ starts easily at the 3-membered P_3-ring. As all efforts to synthesize $P_7(tBu)_3$ have failed so far, we have varied the electronical influence of the substituents of the $PSiR_3$-group [synthesis of $P_7(SiPh_3)_3$, $P_7(SiPh_2Me)_3$, $P_7(SiPhMe_2)_3$]. In all cases the initial complexing occurs at an equatorial P-atom, making sterical reasons for the hampered complexing of $P_7(SiMe_3)_3$ unlikely. The synthesis of $P_7[P(tBu)_2]_3$ (from Li_3P_7 and $(tBu)_2PF$)

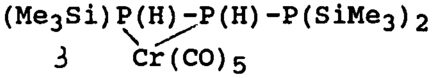
offers the chance to investigate the effect of the PR_2-substituent of the P_7-cage on its complexing properties and thus on the electronic system of this cage. In this case the complexing with $Cr(CO)_5 \cdot THF$ begins on the P-atom of the three membered ring. In order to compare the complexing properties of the differently substituted phosphanortricyclenes to those of similarly substituted di-, tri- and tetraphosphanes the following compounds have been prepared and treated with $Cr(CO)_5THF$: $(Me_3Si)_2P{-}P(tBu)(SiMe_3)$, $(Me_3Si)_2P{-}P(SiMe_3){-}P(SiMe_3)_2$, $(Me_3Si)_2P{-}P(SiMe_3){-}P(SiMe_3){-}P(SiMe_3)_2$, $(Me_3Si)_2P{-}P(H){-}P(tBu)(SiMe_3)$, $(tBu)_2P{-}P(SiMe_3){-}P(tBu)(SiMe_3)$, $(Me_3Si)_2P{-}P(Me){-}P(SiMe_3)_2$, $(Me_3Si)_2P{-}P(Ph){-}P(SiMe_3)_2$. These investigations show, that the complexing preferably occurs at a silylated P-atom or at a hydrogen-substituted P-atom respectively. The reaction of complex 1 with LiBu, yielding 2, and the reaction of 2 with CH_3OH, yielding 3 and 4, demonstrate the increased reactivity of the Si-P-group at a complexed P-atom.


1

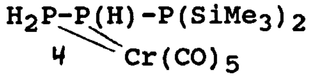
$$\underset{Cr(CO)_5}{(Me_3Si)_2P{-}P(H)}{-}P(SiMe_3)_2$$


2

$$\underset{Cr(CO)_5}{(Me_3Si)P(Li){-}P(H)}{-}P(SiMe_3)_2$$


3

$$\underset{Cr(CO)_5}{(Me_3Si)P(H){-}P(H)}{-}P(SiMe_3)_2$$


4

$$\underset{Cr(CO)_5}{H_2P{-}P(H)}{-}P(SiMe_3)_2$$

After the successful synthesis of $P_7(SiMe_3)_3$ from the reaction of P_4, Na/K with Me_3SiCl and of $P_4(SiMe_2)_3$ (nortricyclene structure) from P_4, Na/K with Me_2SiCl_2, the influence of the molar ratio P_4:Na/K has been thoroughly examined. It could be proven, that at a molar ratio P_4:Na/K = 1:3 the subsequent reaction with R_2SiCl_2 shows a decreased tendency for the formation of the nortricyclene-cage $(R_2Si)_3P_4$, while adamantane structures $(R_2Si)_6P_4$ are considerably favored. The reaction with $Et(Me)SiCl_2$ leads to $[Et(Me)Si]_6P_4$, Et_2SiCl_2 yields $(Et_2Si)_6P_4$ and $PhMeSiCl_2$ generates $[Ph(Me)Si]_6P_4$. This method also enables the synthesis of Si-functional derivatives. Thus the reaction of $Vinyl(Me)SiCl_2$ leads to $[(Vinyl)(Me)Si]_6P_4$, and with $MeHSiCl_2$ $[Me(H)Si]_6P_4$ is obtained. The thermolysis of

$(Me_3Si)_2P\text{-}SiEtMeCl$ allows the formation of chiralic adamantane compounds of the type $[Et(Me)Si]_x(Me_2Si)_{6-x}P_4$, which can be identified by their ^{31}P-NMR-spectra.

The access to PCl-containing triphosphanes enables the formation of iso-tetraphosphanes through the reaction of the corresponding triphosphanes with Li-phosphides. The reactions of triphosphanes of the $R(Me_3Si)P\text{-}P(Cl)\text{-}P(SiMe_3)R'$-type with the Li-phosphides $LiP(SiMe_3)Me$, $LiP(SiMe_3)_2$ and $LiP(SiMe_3)(tBu)$ show, that aside of the basicity of the Li-phosphide the sterical influence of its substituents determines the course of the reaction.
Thus $[Me(Me_3Si)P]_2PCl$ reacts with these 3 phosphides substituting the PCl-group and yielding the respective iso-tetraphosphanes. The more sterically strained triphosphanes $Me(Me_3Si)P\text{-}P(Cl)\text{-}P(SiMe_3)_2$ and $Me(Me_3Si)P\text{-}P(Cl)\text{-}P(SiMe_3)(tBu)$ also react with $LiP(SiMe_3)_2$ or $LiP(SiMe_3)(tBu)$ to the corresponding iso-tetraphosphanes, but the reaction with the more reactive $LiP(SiMe_3)Me$ preferably leads to the cleavage of the P-P-bond. The similarly sterically hindered triphosphanes $[(Me_3Si)_2P]_2PCl$, $(Me_3Si)_2P\text{-}P(Cl)\text{-}P(SiMe_3)(tBu)$ and $[(tBu)(Me_3Si)P]_2PCl$ do no longer react with the mentioned Li-phosphides in the sense of substituting the PCl-group. Instead they undergo cleavage of a $P\text{-}SiMe_3$-bond and thus form lithiated triphosphanes ($Li/SiMe_3$-exchange). For example $[(tBu)(Me_3Si)P]_2PCl$ reacts with $LiP(SiMe_3)(tBu)$ to $P(SiMe_3)_2(tBu)$ and $(tBu)(Li)P\text{-}P(Cl)\text{-}P(SiMe_3)(tBu)$. The latter eliminates LiCl and forms the triphosphene $(tBu)(Me_3Si)P\text{-}P{=}P(tBu)$, which finally undergoes dimerisation to either cis- or trans-cyclotetraphosphane $P_4[P(SiMe_3)(tBu)]_2(tBu)_2$.
While PCl-containing, silylated di- and triphosphanes are very reactive and easily undergo different subsequent reactions, PF-substituted derivatives prove to be considerably more stable. However, with Li-phosphides they

do not give the substitution of the PF-group, but rather undergo cleavage of the Si-P- or P-P-bond. Fluorinated triphosphanes, like $[(Me_3Si)_2P]_2PF$, are accessible through the reaction of $F_2P-P(SiMe_3)_2$ with $LiP(SiMe_3)_2$. $F_2P-P(SiMe_3)_2$ is obtained by both the reaction of $BrPF_2$ + $P(SiMe_3)_3 \rightarrow F_2P-P(SiMe_3)_2 + Me_3SiBr$, and the reaction of $BrPF_2$ with $LiP(SiMe_3)_2$. The reaction of a lithiated triphosphane with PF_3 allows the introduction of the PF_2-group forming the iso-tetraphosphane $F_2P-P[PSiMe_3)(tBu)]_2$.

Lithiated diphosphanes, like $Li(Me_3Si)P-P(SiMe_3)(tBu)$ react with 1,2-dibromoethane to give tetraphosphanes. The corresponding reaction of the triphosphane $[(tBu)_2P]_2PLi$ does not take place analogously. Instead at 20°C $(tBu)_2PBr$, LiBr and the cyclophosphanes $P_4[P(tBu)_2]_4$ and $P_3[P(tBu)_2]_3$ are formed, while C_2H_4 is generated. At -40°C it is possible to isolate the intermediate $(tBu)_2P-P=P(tBu)_2Br$. LiBr, which at 20°C decomposes to give the mentioned endproducts. In the course of this reaction the phosphinophosphinidene $(tBu)_2P-P$ is generated as another intermediate, which could be identified by trapping reactions with either 2,3-dimethyl-1,3-butadiene or cyclohexene [5].

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