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SYNTHESIS AND REACTIONS OF PHOSPHORUS-RICH SILYLPHOSPHANES

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I. Introduction

After having prepared $H_3Si—PH_2$ (*1*) from SiH_4 and PH_3, our interests were extended to the reaction possibilities of the P—H and SiH groups, especially the properties of the Si—P bond and the behavior of the free electron pairs. The Si—P bond appeared to be easily cleaved with HBr or alcohol (*2*), with aluminum halides (*3*), BCl_3 (*4*), and other element halides, as well as with acid chlorides (*5*), or $COCl_2$ (*6*). The easy transferability of the phosphane groups to other elements hence became possible and was used in the preparation of element–phosphorus compounds. In organo-substituted silylphosphanes the Si—P bond is the only reactive bond. The reaction with EtI, and the corresponding one with HI, takes place with the formation of Me_3SiI and $(Et_4P)I$ if an excess of EtI is used. During the reaction at −78°C equimolar amounts of the adducts $Me_3Si—PEt_2 \cdot EtI$, and $Me_3Si—PEt_2 \cdot HI$ are formed. These, when warmed, react by cleavage of the Si—P bond (*7*). Similar adducts are formed with $AlCl_3$ and BCl_3, which, when warmed, also react by cleavage of the Si—P bond and by formation of the element–phosphorus bond (*3, 4*). In silylated transition metal complexes the formation of silylphosphonium compounds like $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ or $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ from $Mw_3SiCo(CO)_4$ and Me_3P, or $Me_3Si—PMe_2$, respectively, can also be observed (*8*).

The capacity to form phosphonium salts decreases when negatively charged substituents are introduced at the silicon atom. Thus, with $F_3Si—PH_2$, only a slight tendency to form adducts and to split the Si—P bond is observed (*9*). Silylphosphanes with a PH_2 group like

Me_3SiPH_2 or $H_3Si—PH_2$ can be metallated with $LiPEt_2$ without splitting the Si—P bond (*10*).

$$H_3Si—PH_2 + 2LiPEt_2 \longrightarrow H_3Si—PLi_2 + 2HPEt_2$$

Through reaction with CH_3Cl, $H_3Si—PMe_2$ can then be formed. Compounds of the type $H_{3-x}Me_xSi—PHLi$ can be obtained from the reaction of the PH_2-containing derivative with LiPHMe (*10*), according to

$$H_3Si—PH_2 + LiPHMe \longrightarrow H_3Si—PHLi + MePH_2$$

These undergo disproportionation at room temperature in ether solution according to

$$2H_3Si—PHLi \longrightarrow (H_3Si)_2PLi + LiPH_2$$

Whereas SiH-containing silylphosphanes such as $H_3Si—PEt_2$ react with $LiPEt_2$ by substituting the SiH group, lithium alkyls on the other hand cleave the Si—P bond (*11*) as shown in the following case.

$$HSi(PEt_2)_3 + LiMe \longrightarrow MeSiH(PEt_2)_2 + LiPEt_2$$

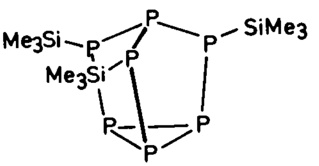
This finding led to the question, how far in multiply silylated silylphosphanes can Si—P bonds be formed from the cleavage reactions. This was investigated on $P(SiMe_3)_3$ (*12*). At −40°C in THF the reaction with LiBu proceeds practically completely according to:

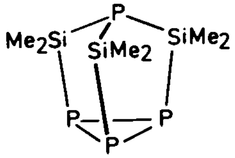
$$P(SiMe_3)_3 + LiBu \xrightarrow{THF} LiP(SiMe_3)_2\ 2THF + BuSiMe_3$$

$LiP(SiMe_3)_2{\cdot}2THF$ (white crystals) is outstandingly suitable for the transfer of the $P(SiMe_3)_2$ group, and hence for the preparation of various phosphorus-element compounds (*13*).

$$LiP(SiMe_3)_2 + CH_2Cl_2 \longrightarrow (Me_3Si)_2P—CH_2—P(SiMe_3)_2$$
$$LiP(SiMe_3)_2 + Me_2SiCl_2 \longrightarrow (Me_3Si)_2P—SiMe_2—P(SiMe_3)_2$$
$$LiP(SiMe_3)_2 + Me_2NBCl_2 \longrightarrow (Me_3Si)_2P—B(NMe_2)—P(SiMe_3)_2$$

Therefore our interest focused on $(Me_3Si)_3P$; the first step was to find a suitable approach to prepare this compound. This turned out to be the reaction of white phosphorus with Na/K alloy and then with Me_3SiCl (*14*). The formation of $(Me_3Si)_3P$ is based upon the phosphide Na_3P. Accordingly, complete cleavage of the P_4 structure by means of the alkali must have occurred. The next step was to decrease the relative amount of the alkali metal in order to prevent the complete cleavage of the P_4 structure as a prerequisite for the formation of phosphorus-rich phosphides. By reaction of the latter with Me_3SiCl it was believed that phosphorus-rich silylphosphanes should become available. Our further investigations confirmed this hypothesis and resulted in the formation, among other compounds, of $(Me_3Si)_3P_7$ (*15*) and $(Me_2Si)_3P_4$ (*16*).





But these are not the only products of the reactions. Other phosphorus-rich compounds, [e.g., $(Me_3Si)_4P_{14}$] were obtained. It appeared reasonable to assume a corresponding phosphide to serve as a basis for the formation of $(Me_3Si)_3P_7$. Subsequently, Li_3P_7 became available as one example of these phosphides through the work of M. Baudler on the reaction of diphosphane with $LiPH_2$ (*17*). Soon thereafter, both Bauder's group (*18*) and our own research group (*19*) obtained this phosphide from white phosphorus.

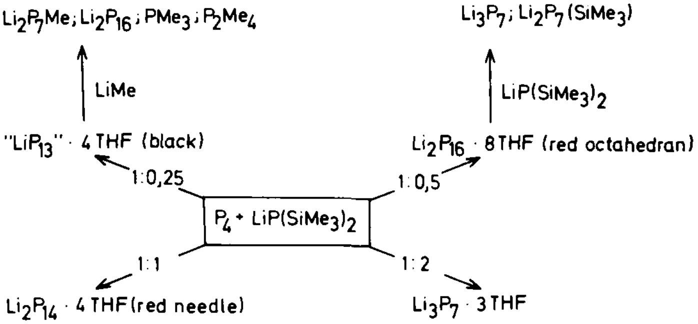
The investigation of the reaction of the silylated diphosphane $P_2(SiMe_3)_4$ in THF with $LiCMe_3$ showed that Li_3P_7 is also formed among other compounds, through a series of complex reactions from the initially formed $Li(Me_3Si)P—P(SiMe_3)_2$ (*20*).

Our present knowledge of the chemistry of the phosphorus compounds and in particular of the chemistry of the silylphosphanes is not sufficient for a full understanding and explanation of these complicated reactions in every detail. The investigations reviewed in this article were all undertaken to broaden the basic knowledge in this field with the final goal of permitting a full understanding of these reactions.

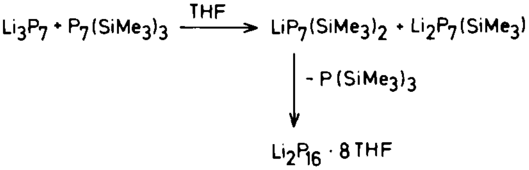
II. Formation of $P_7(SiMe_3)_3$

In the reaction of white phosphorus with lithium alkyls, poorly soluble phosphides are first formed, and are subsequently degradated by organometallic compounds. In this degradation, unsubstituted phosphides like Li_3P_7 are formed, as well as partially alkylated phosphides such as $LiP_7(CMe_3)_2$, $Li_2P_7(CMe_3)$, $LiP(CMe_3)_2$, and $LiP_4(CMe_3)_3$ (using $LiCMe_3$) (*19*). The influence of the concentration ratios on the formation of the compounds which result from the reaction of P_4 with

$LiP(SiMe_3)_2$ (*21*) can be seen in Scheme 1. Li_3P_7 reacts with $P_7(SiMe_3)_3$ according to Scheme 2.

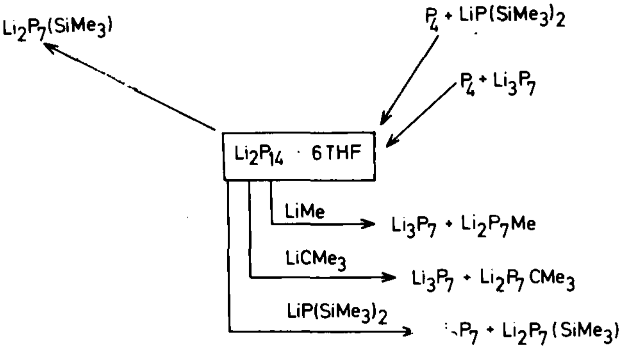


SCHEME 1



SCHEME 2

Li_2P_{16}·8THF results from the reaction between P_4 and $LiPH_2$·THF as M. Baudler and co-workers (*22*) were the first to demonstrate. It is also formed in the reaction between P_4 and LiMe or $LiCMe_3$. Whereas $LiP_7(SiMe_3)_2$ yields Li_2P_{16} as $P(SiMe_3)_3$ is split off, $Li_2P_7(SiMe_3)$ reacts to form Li_2P_{14}. The possible pathways for the synthesis of Li_2P_{14} and its reactions are summarized in Scheme 3.



SCHEME 3

Finally, it is possible to obtain phosphorus-rich phosphides by the reaction of P_4 with Li_3P_7:

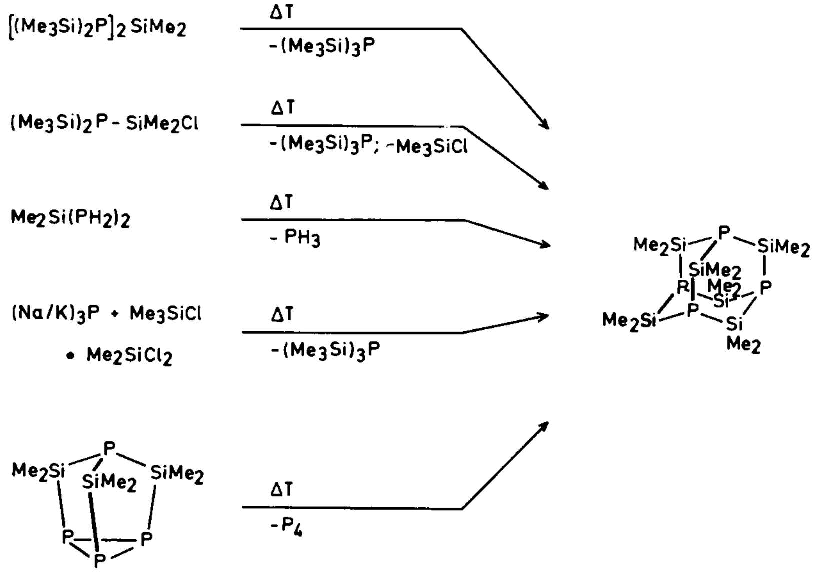
$$Li_2P_{14}\,;\,Li_2P_{16} \xleftarrow{1:1} \boxed{P_4 + Li_3P_7} \xrightarrow{4:1} Li_2P_{16}\,;\,\text{"}LiP_{13}\text{"}$$

These equations are deduced from the reactions of every phosphide isolated. The interests in the field of P_7 and related systems of the research group of M. Baudler and those of our own, which are similar but complementary, developed initially from different approaches to the problem. To clarify the structure of the phosphides obtained we tried, though without satisfactory results, to form single crystals suitable for X-ray structural analysis. On the other hand the group of M. Baudler was able to determine the structure of Li_3P_7, Li_2P_{16}, Li_2P_{14} in solution by means of the highly sophisticated ^{31}P-NMR spectroscopy.

From the findings presented concerning the reactions of P_4 it follows that the formation of Li_3P_7 and therefore also of $P_7(SiMe_3)_3$ takes place in several interrelated reaction steps which influence one another, but which cannot yet be detailed. We lack both a detailed picture of the reactive behavior of these compounds and a reliable knowledge of the first steps of the formation reactions. Therefore we sought to understand the problem by investigating simpler systems able to help in its solution. A report of this approach now follows.

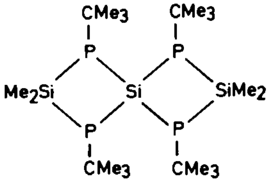
III. Formation of Cyclic Silylphosphanes

The reactions of alkali phosphides with R_2SiCl_2 opened the way to the chemistry of the cyclic silylphosphanes. Thus Parshall and Lindsey (*23*) were the first to report the formation of $Et_2Si(PR)_2SiEt_2$ (R = H, Ph, $SiMe_3$) by reaction of the corresponding lithium phosphide with Et_2SiCl_2, or with the bicyclic compound $P(SiEt_2)_3P$. Schumann and Benda (*24*) described the compounds $(PhP—SiPh_2)_3$ and $(PhP—SiPh_2)_2$, and West *et al.* (*25*) obtained $(PhP—SiMe_2)_2$ and $(PhP—SiMe_2)_3$ by reacting $KHPPh/K_2PPh$ with Ph_2SiCl_2, or Li_2PPh with Me_2SiCl_2, respectively. From the reaction of K_2PPh with $PhSiCl_3$, Schumann and Benda (*26*) described the formation of $(PPh)_6(SiPh)_4$, which has an adamantane structure. In clear contrast to these seemingly obvious reactions is the formation of cyclic silylphosphanes by rearranging linear silylphosphanes such as $[(Me_3Si)_2P]_2SiMe_2$ to yield the four-membered ring $(Me_3SiP—SiMe_2)_2$ after $(Me_3Si)_3P$ is split off (*27*), and the preferred formation of $P_4(SiMe_2)_6$ (adamantane structure) as shown in Scheme 4.

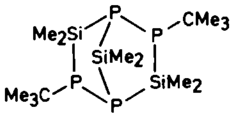


SCHEME 4

Reactions of LiPH(CMe_3) with R_2SiCl_2 (R = Ph, Me, CMe_3) lead to (Me_2Si—PMe)$_3$, [(Me_3C)$_2$Si—PMe]$_2$, $Me_2Si(P—CMe_3)_2SiPh_2$, and the following (*28, 29*):

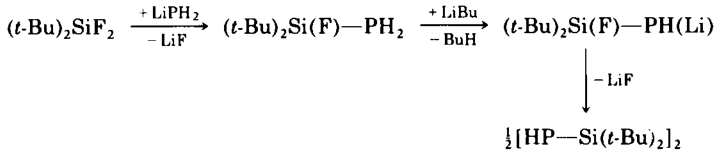


and



Finally, the reactions of P_4 with Na/K alloy and Me_2SiCl_2 for the preparation of the trisilatetraphosphanortricyclene $P_4(SiMe_2)_3$, and of $(Me_3Si)_3P_7$ (*15, 16*), must be mentioned.

The reactions of lithium phosphides with chlorosilanes, which initially seemed so straightforward, turned out to be strikingly many-sided when PH-containing lithium phosphides are present. The formation of pure $LiPH_2 \cdot DME$ (DME = 1,2-dimethoxyethane) became feasible by coordination of a high boiling point ether (*30*). This method was employed by Klingebiel and collaborators (*31*) for the formation of cyclic phosphanes, according to the following scheme:



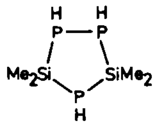
$$(t\text{-Bu})_2SiF_2 \xrightarrow[-LiF]{+LiPH_2} (t\text{-Bu})_2Si(F)\text{—}PH_2 \xrightarrow[-BuH]{+LiBu} (t\text{-Bu})_2Si(F)\text{—}PH(Li) \xrightarrow{-LiF} \tfrac{1}{2}[HP\text{—}Si(t\text{-Bu})_2]_2$$

Correspondingly, by reacting R_2SiF_2 with $LiPH(CMe_3)$, these workers produced $[(Me_3C)P\text{—}SiR_2]_2$ [R = CMe_3,—$NMe(SiMe_3)$].

A. Reactions of Lithium Phosphides with Me_2SiCl_2

The possible reactions of the lithium phosphides Li_3P, Li_2PH, and $LiPH_2$ with Me_2SiCl_2 are largely determined by the PH groups present. The compounds Li_3P and Na_3P prepared by melting the elements together are well known from the research of Brauer and Zintl (*32*). Since these substances cannot be used in organometallic reactions because of their low solubility, the metallation of PH_3 with LiBu in ether solution was repeatedly applied to obtain the lithium phosphides. This method was also employed by Parshall and Lindsey to prepare $P(SiEt_2)_3$ (*23*). But these brownish yellow substances often present several disadvantages: (1) they still contain LiBu, if applied in excess, as well as the Li_3P formed (*33*); (2) the metallation of PH_3 is not complete; and (3) they consist of a mixture of PH-containing lithium phosphides.

If for the reaction of Me_2SiCl_2 at 0°C a lithium phosphide is used, the latter formed by the introduction of excess PH_3 in LiBu/hexane/Et_2O



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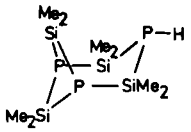

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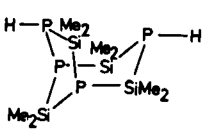

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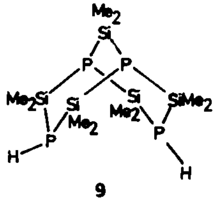

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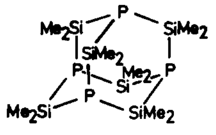

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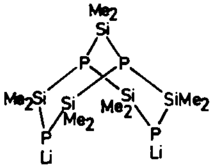
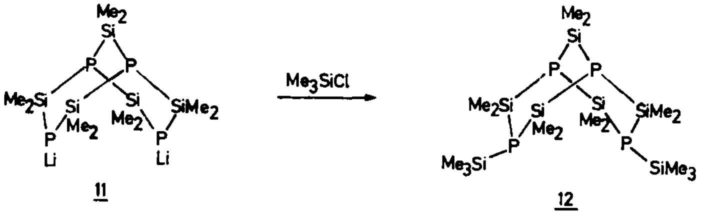
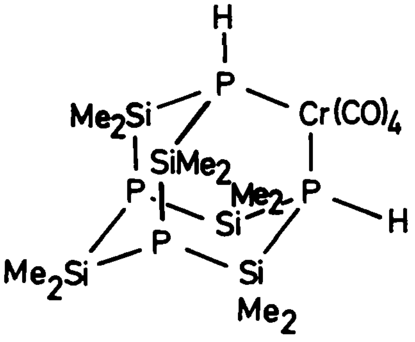


11

solution (yellow suspension), the reaction products are (*34*) $Me_2Si(PH_2)Cl$ (**1**), $Me_2Si(PH_2)_2$ (**2**), $H_2P—SiMe_2—PH—SiMe_2Cl$ (**3**), $(H_2P—SiMe_2)_2PH$ (**4**), compound **5**, $(HP—SiMe_2)_3$ (**6**), and compounds **7**–**11**; compounds **9** and **10** as well as **6** and **7** are the principal products. The reaction of Me_2SiCl_2 with excess lithium phosphides produces further metallation of the PH groups and favors formation of polycyclic compounds, as can be perceived by the increase in the concentration of **10** among the reaction products. Besides compound **9** the lithiated derivative **11** is also formed. This can be isolated as an orange-yellow powder and may be transformed by means of Me_3SiCl into the silylated compound **12**. The bicyclic compound **8** is a by-product of this reaction.



The X-ray structural analysis of compound **9** has been performed (*35*). Compound **9**, a precursor of **10**, reacts with $(CO)_4CrNBD$ (NBD = 7-nitrobenzo-2-oxa-1,3-diazole) to form the following compound:



1. Reaction of Li_2PH *with* Me_2SiCl_2

Nearly pure Li_2PH is obtained from the reaction of 1:1 molar proportions of $LiPH_2 \cdot DME$ and LiBu.

$$LiPH_2 + LiBu \longrightarrow Li_2PH + BuH$$

The reaction of Li_2PH in DME leads preferentially to compounds **9** and **10**, which appear as a white powder, from which compound **9** can be obtained as cubic crystals by recrystallization with pentane or toluene. The presence of $Me_2Si(PH_2)Cl$ (**1**), $Me_2Si(PH_2)_2$ (**2**), as well as **3**, **4**, **5**, **6**, **7**, and **8** can be demonstrated in the liquid products of the reaction (*34*).

The reaction in pentane with a small admixture of DME progresses considerably slower, but yields, besides compound **10**, principally the same products as obtained in pure DME.

2. *Reactions of* Li_3P *with* Me_2SiCl_2

It was not possible to obtain Li_3P by metallation of $LiPH_2$ with LiBu due to an ether cleavage reaction. Its formation succeeded through the reaction of PH_3 with an excess of LiBu in a solution of hexane/toluene and through the repeated action of LiBu on the lithium phosphide obtained initially (*34*).

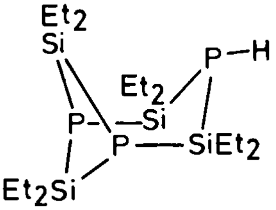
The reaction of this Li_3P with Me_2SiCl_2 in a molar ratio of 1:2 progresses very slowly in DME. After 12 hours at 0°C the suspension of the reaction mixture still has a light brown color. It is only after a 4-hour heating at 84°C that this color slowly clears up. During the reaction, compound **10** (adamantane structure) is formed, as well as small quantities of by-products. There was no indication of the formation of $P(SiMe_2)_3P$.

3. *Reaction of* $LiPH_2 \cdot DME$ *with* Me_2SiCl_2

In the course of the reaction of $LiPH_2 \cdot DME$ with Me_2SiCl_2 in DME in a molar ratio 2:1 at a temperature of $-40°C$, about 55 mol% of the phosphorus employed is converted to PH_3. The white product that separates contains compound **10** and LiCl. Further concentration of the filtrate causes precipitation of still more compound **10**, accompanied by the evolution of PH_3. The main products of the reaction are PH_3 and compound **10** (*34*).

B. REACTION OF LITHIUM PHOSPHIDES WITH Et_2SiCl_2

The lithium phosphide used (by analogy with Section III,A) reacts with Et_2SiCl_2 in hexane/pentane at 20°C only very slowly. Only after 36 hours does the phosphide suspension lose its color. In addition to LiCl, it was possible to detect compound **13**. On the other hand, formation of compounds **10** and **11** did not take place. By distilling the filtrate the following compounds were separated or at least concentrated in fractions: $Et_2Si(PH_2)Cl$(**14**) (main product), $Et_2Si(PH_2)_2$ (**15**), $(ClEt_2Si)_2PH$ (**16**), $ClEt_2Si—PH—SiEt_2—PH_2$ (**17**), $(H_2P—SiEt_2)_2PH$ (**18**), $(HP—SiEt_2)_2$ (**19**), and $(HP—SiEt_2)_3$ (**20**). Compounds, **18**, **19**, and **20** could be separated by means of high-pressure liquid chromatography (HPLC) (*34*). Evidence for the presence of $P(SiEt_2)_3P$ was impossible to find. Reaction of the above-mentioned lithium phosphide with Et_2SiCl_2 in Et_2O yielded principally the same compounds, albeit in quantitatively different proportions. In addition, the five-membered ring **21** was observed in small amounts. The compounds **15** (30%) and **18** (10%) are formed as principal products; these were already present in the reaction mixture. Yet neither the four-membered ring **19** nor the six-membered ring **20** is formed. These can first be found in the fractions separated by means of distillation, in which the quantity of **20** then amounts to ~10% of the total silylphosphanes obtained. Derivatives of compounds **10** and **11**, as well as $P(SiEt_2)_3P$, are not formed (*34*).



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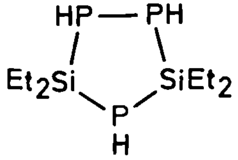

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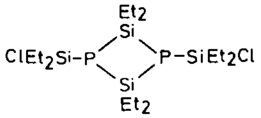
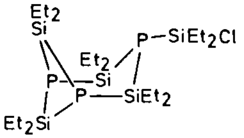
The reaction of Li_3P (formed from PH_3 and LiBu) with Et_2SiCl_2 in a molar ratio of 2:3 in ether at room temperature progresses only very slowly. After 1 hour compound **13** can be detected among the compounds formed. The reaction in toluene at 20°C shows only little progress after 3 days; after heating at 110°C during 8 hours, the following compounds are formed:





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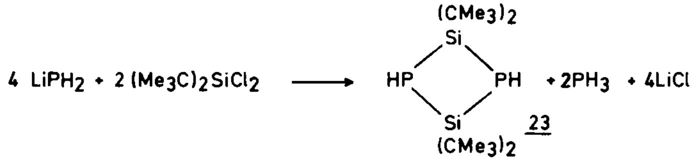
In addition, the butylated compounds $ClEt_2SiP(SiEt_2)_2—PSiEt_2Bu$ and $(SiEt_2)_4P_3SiEt_2Bu$ (the butylated derivative of **22**), and trace amounts of **13** are formed. A compound with the adamantane structure corresponding to compound **10** or to its precursor **11** can be excluded with certainty.

C. Reactions of $LiPH_2 \cdot DME$ and Li_2PH with $(Me_3C)_2SiCl_2$

Introduction of the sterically important Me_3C group favors the formation of the four-membered ring. The reaction of $(Me_3C)_2SiCl_2$ with $LiPH_2 \cdot DME$ at −70°C in a molar ratio of 1.2:2 results in the formation of compound **23**, which was isolated with a yield of 76% in the form of white crystals as shown in Eq. (1). The elimination of PH_3 begins during addition of $LiPH_2$ solution at −70°C; 35% of the phosphorus introduced is converted to PH_3. This corresponds to the formation of compound **23** with a yield of 70%. At the end there remains a viscous liquid which contains $(Me_3C)_2SiCl_2$, $(Me_3C)_2Si(PH_2)_2$ (**24**), and $(t\text{-}Bu)_2Si(PH_2)Cl$ (**25**) (*34*).



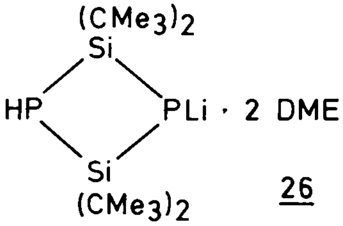
(1)

The reaction of Li_2PH with $(Me_3C)_2SiCl_2$ proceeds very slowly indeed (at 20°C and not before 16 hours have elapsed), to yield compound **23** according to

$$2Li_2PH + 2(Me_3C)_2SiCl_2 \longrightarrow HP[Si(CMe_3)_2]_2PH + 4LiCl$$

1. *Lithiation and Substitution of* $HP[Si(Me_3)_2]_2PH$

The reaction of **23** with $LiPH_2$ in DME yields preferentially compound **26** and PH_3. Even with an excess of $LiPH_2$ (molar ratio 1:2) lithiation of the second PH group cannot be achieved. The reaction of $HP[Si(CMe_3)_2]_2PH$ with LiBu in DME leads to the isolation of **26** in the form of colorless crystals (reaction yield 40%), which are found in the reaction mixture together with unreacted **23**; however, it does not entail the formation of $LiP[Si(CMe_3)_2]_2PLi$ (**27**). Increasing the LiBu concentration merely promotes the cleavage of DME. The best approach to the



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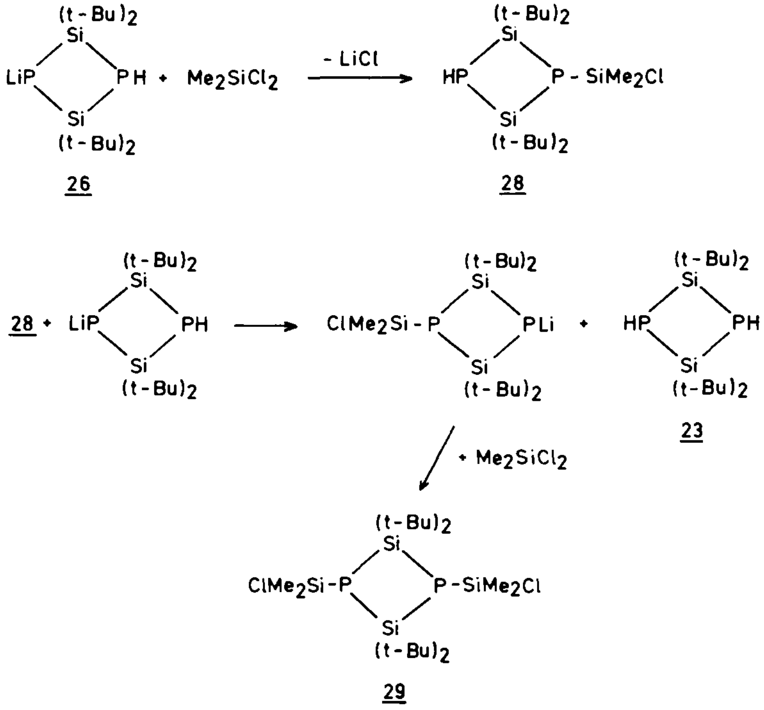
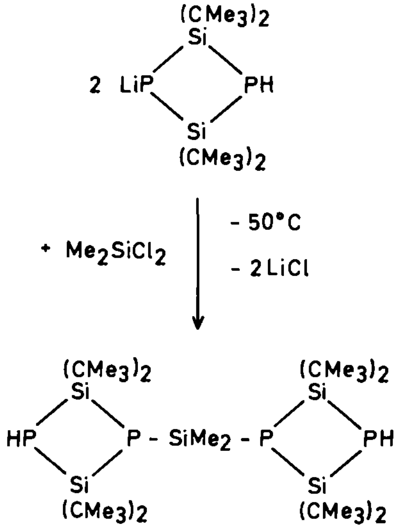


SCHEME 5

preparation of compound **26** is reaction of **23** with $LiCMe_3$ (molar ratio 1:1 in toluene or pentane/hexane, reaction time 2 days). Since compound **26** is only moderately soluble in these hydrocarbons, it precipitates as a white power (yield 76%). The ether-free compound **26** ignites spontaneously in air and is very soluble in THF. It dissolves in DME if warmed, and it crystallizes out of this solution as $LiP[Si(CMe_3)_2]_2PH \cdot 2DME$. With considerable excess of Me_2SiCl_2, compound **26** forms, at −70°C in DME, a mixture of the following compounds: $HP[Si(CMe_3)_2]_2P—SiMe_2Cl$ (**28**) (83%), $ClMe_2Si—P[Si(CMe_3)_2]_2P—SiMe_2Cl$ (**29**) (10%), and $HP[Si(CMe_3)_2]_2PH$ (**23**) (7%) (percentages are obtained by integrating the ^{31}P-NMR spectra).

Formation of **29** and **23** is due to the transmetallation reaction shown in Scheme 5. By means of fractional crystallization it has been possible to isolate compound **29** in the form of colorless crystals. If the solution obtained by the metallation of **23** with LiBu at −70°C is added to Me_2SiCl_2 at −50°C, compound **30** is obtained as shown in Eq. (2).



(2)

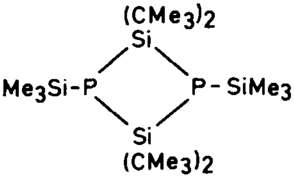
30

Compound **30** separates as a snow white glistening powder. It dissolves well in THF and toluene, poorly in DME and benzene. By metallation of the PH group in compound **28** with LiBu it is not possible to obtain an additional ring closure by elimination of LiCl to yield the corresponding bicyclic molecule. Undetermined molecular associations occur instead.

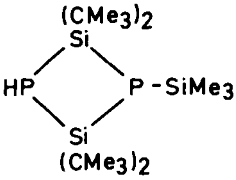
Reactions of **23** with $LiCMe_3$ in a molar ratio 1:4 in pentane at 20°C (reaction time 24 hours) indicate that metallation of the second PH group in **26** to yield $LiP[Si(CMe_3)_2]_2PLi$ (**27**) is possible. A white solid is formed in this reaction, and the consumption of $LiCMe_3$ corresponds to a double lithiation of compound **23**. There are signs that the dilithiated compound **27** is characterized in the ^{31}P-NMR spectrum by $\delta = -280$ ppm, but it has been impossible to obtain compound **27** in a pure form despite repeated metallation reactions.

The reaction of **23** with $LiCMe_3$ in pentane in a 1:4 molar ratio produces a phosphide, which, besides compound **27**, still contains some **26**. The latter can be further metallated by repeated reactions with LiBu so that an enriched end product is obtained whose content of compound **27** is about 80% (*36*).

The reaction of a lithiated product (free of compound **23**) with Me_3SiCl yields compounds **31** (62%), **32** (31%), and **23** (7%). Compound **23** is obtained by transmetallation.



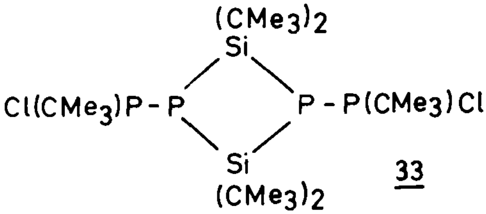
31



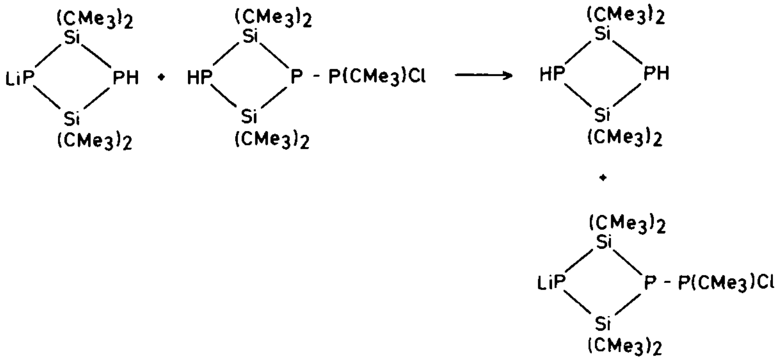
32

2. *Reactions of* $LiP[Si(CMe_3)_2]_2PH$ *and* $LiP[Si(CMe_3)_2]PLi$ *with* Me_3CPCl_2

The mixture of compounds **26** and **27** (about 30% **26**) reacts in hexane with *t*-$BuPCl_2$ and yields as the principal product compound **33** (yellow, needle-shaped crystals, easily soluble in pentane and cyclohexane). It also yields compound **23**. Compound **33** is formed in the cis and the trans configuration. The formation of **23** is due to the transmetallation shown in Eq. (3). The analogous reaction in THF yields the compounds $HP[Si(CMe_3)_2]_2P{-}P(CMe_3){-}P[Si(CMe_3)_2]_2PH$ (**36**) (main product), $HP[Si(CMe_3)_2]_2P{-}P(CMe_3)H$ (**37**), $HP[Si(CMe_3)_2]_2P{-}P(CMe_3)_2$ (**38**), as well as $Cl(CMe_3)P{-}P[Si(CMe_3)_2]_2P{-}P(CMe_3)Cl$ (**33**), $H(CMe_3)P{-}P[Si(CMe_3)_2]_2P{-}P(CMe_3)Cl$ (**34**), and $H(CMe_3)P{-}P[Si(CMe_3)_2]_2P{-}P(CMe_3)H$ (**35**).



33



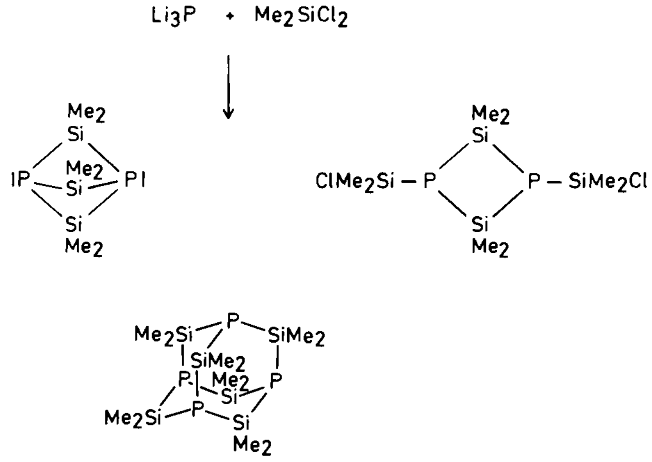
(3)

Formation of compounds **34**, **35**, and **37** is explained by Li/Cl exchange, which results from the incomplete metallation of compound **23**, since in the reaction mixture $LiCMe_3$ persists as metallating reagent. This attacks the compounds having a terminal $P(CMe_3)Cl$ group by Li/Cl exchange and generates a $P(CMe_3)Li$ group and Me_3CCl. The latter reacts by forming $P(CMe_3)H$, $Me_2C{=}CH_2$, and LiCl. Compound **38** results from the reaction of $HP[Si(CMe_3)_2]_2$-$P{-}P(CMe_3)Cl$ (**39**) with excess $LiCMe_3$ (*36*).

3. *The Compound* $P(SiMe_2)_3P$

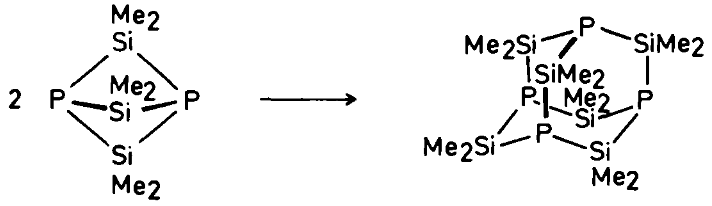
In 1959 Parshall and Lindsey published their findings concerning the reactions between Li_3P and Et_2SiCl_2, and reported the formation of the bicyclic compound $P(SiEt_2)_3P$ (*23*).

This compound, which was not completely described at that time, has never been prepared again nor examined by any research group. We were unsuccessful for a long time. But after we had recognized the difficulties which can occur in the reactions of lithium phosphides with R_2SiCl_2, we turned back to Li_3P prepared from elemental lithium and phosphorus. It was suspended in toluene and at 20°C was stirred during 9 or 10 days together with Me_2SiCl_2. The bicyclic compound $P(SiMe_2)_3P$ was formed, along with $ClMe_2Si{-}P(SiMe_2)_2P{-}SiMe_2Cl$ and trace amounts of $P_4(SiMe_2)_6$ (adamantane) (*37*) (Scheme 6). The bicyclic compound can be distilled off at 110°C/10^{-3} Torr. It is a



SCHEME 6

liquid, which decomposes to adamantane at a slightly higher temperature [Eq. (4)].



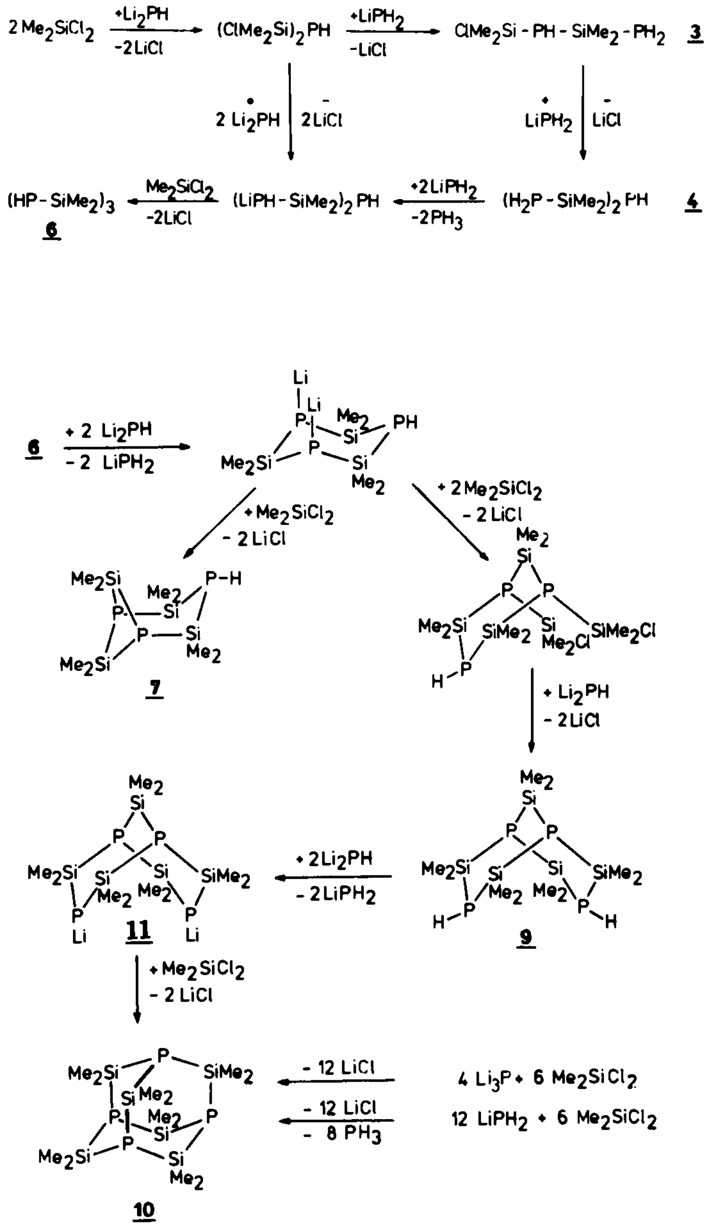
(4)

D. DISCUSSION OF RESULTS

The investigations performed show that the reactions of the PH-containing phosphides $LiPH_2$ and Li_2PH, or of their mixtures with Li_3P (all prepared from PH_3), with Me_2SiCl_2 lead to compound **10** with an adamantane structure. The intermediate products are a series of cyclic silylphosphanes. Compound **10** is always the main product of the reaction if Me_2SiCl_2 is reacted with an excess of lithium phosphide. For the single reaction steps a transmetallation mechanism can be formulated. This may be recognized both by the evolution of PH_3 during the reactions with $LiPH_2$ and by the isolation of the lithiated compound **11** (formed from compound **9**).

At first the fact that the formation of the bicyclic compound $P(SiMe_2)_3P$ could not be observed seemed incomprehensible. An explanation can be that this compound, under the given reaction conditions, reacts further to form compound **10**. But compound **10** cannot be formed only in this way, as is demonstrated by the isolation of its precursor **9** and of the lithiated compound **11**, which should react with Me_2SiCl_2 to form **10**. Compound **10** is doubtlessly a favored molecule in the series of these cyclic silylphosphanes.

The influence of the substituents on ring size of the reaction products and on the further reactions leading to the formation of polycyclic silylphosphanes is particularly striking. Whereas in the reaction with Me_2SiCl_2 the four-membered ring $(HP—SiMe_2)_2$ was absolutely impossible to obtain and the four-membered ring structure appeared only in the bicyclic compound **7**, in the reactions with Et_2SiCl_2 the four-membered ring $(HP—SiEt_2)_2$ and the six-membered ring $(HP—SiEt_2)_3$ proved to be the favored products. Experimental results indicate that compounds **19** and **20** are formed from the PH-containing linear silylphosphanes only when the reaction products undergo thermal treatment (distillation). In the case of the reation with $(Me_3C)_2SiCl_2$, the main product is $HP[Si(CMe_3)_2]_2PH$ and the six-membered ring no


2 Me2SiCl2
+Li2PH
-2LiCl
(ClMe2Si)2PH
+LiPH2
-LiCl
ClMe2Si - PH - SiMe2 - PH2
3
+ 2 Li2PH
- 2LiCl
+ LiPH2
- LiCl
(HP-SiMe2)3
6
Me2SiCl2
-2LiCl
(LiPH-SiMe2)2PH
+2LiPH2
-2PH3
(H2P-SiMe2)2PH
4
6
+ 2 Li2PH
- 2 LiPH2
+ Me2SiCl2
- 2 LiCl
+ 2Me2SiCl2
- 2 LiCl
7
+ Li2PH
- 2LiCl
+ 2Li2PH
- 2LiPH2
11
9
+ Me2SiCl2
- 2 LiCl
- 12 LiCl
- 12 LiCl
- 8 PH3
4 Li3P + 6 Me2SiCl2
12 LiPH2 + 6 Me2SiCl2
10

SCHEME 7

longer appears. Compounds **9** and **10**, so strongly favored in the reactions with Me_2SiCl_2, are certainly not formed—under the chosen reaction conditions—in the reactions with Et_2SiCl_2 or $(Me_3C)_2SiCl_2$, respectively. Undoubtedly this depends upon the silicon substituents. Nevertheless, the question remains unanswered whether the failure to format these compounds derives from the deficiency of the corresponding precursor, or whether the formation of an Si—P adamantane with phosphorus atoms in the bridge-head positions and bulky substituents on the Si atoms presents difficulties.

The importance of the intermediate reactions which occur within the overall reaction can be deduced from the multiplicity of the compounds formed during the reaction of $LiPH_2$ or Li_2PH with Me_2SiCl_2. This can, in principle, also be seen in the reaction of $LiPH_2$ with $(Me_3C)_2SiCl_2$ to yield $HP[Si(CMe_3)_2]HP$. The PH_3 obtained can arise by lithiation of a PH-containing intermediate by $LiPH_2$. In this way, $(Me_3C)_2Si(PH_2)_2$, for example, can yield $(Me_3C)_2Si(PHLi)_2$ and PH_3, and react further with $(Me_3C)_2SiCl_2$ to form $HP[Si(CMe_3)_2]_2PH$ and LiCl. The analogous compound $Et_2Si(PH_2)_2$ has also been obtained.

These two reactions, the substitution with elimination of LiCl and the PH lithiation by lithium phosphides, explain the formation of the compounds obtained in the reaction of Me_2SiCl_2 according to the reaction scheme of Scheme 7, in which all identified compounds are given a number.

By metallation of **23** with $LiCMe_3$ the formation of pure $LiP[Si(CMe_3)_2]_2PLi$ (**27**) can never be achieved; instead, a mixture of $HP[Si(CMe_3)_2]_2PLi$ (**26**) and (**27**) (as much as 80%) is obtained. The reactions of these lithiated derivatives of **23** with chloro silanes (Me_2SiCl_2 and Me_3SiCl) or with Me_3CPCl_2 are determined by substitution and transmetallation reactions. These phenomena permit the explanation of the formation of the compounds obtained. Synthesis of a bicyclic compound by further ring closure (e.g., by metallation of **28** and ring closure with elimination of LiCl) is not possible, because the linking to form "chains of rings," as in **30** or **36**, is favored.

IV. Synthesis and Reactions of Silylated Triphosphanes and Triphosphides

$LiP(SiMe_3)_2 \cdot 2THF$ (**12**), which was formed from $(Me_3Si)_3P$ and lithiating agents, proved to be the appropriate reagent for the transfer of the $P(SiMe_3)_2$ group and therefore made possible the preparation of phosphorus functional compounds such as $[(Me_3Si)_2P]_2SiMe_2$. The reaction of $LiP(SiMe_3)_2 \cdot 2THF$ with PCl_3 progresses through

$(Me_3Si)_2P—PCl_2$ to yield $[(Me_3Si)_2P]_2PCl$, which with $LiCMe_3$ forms $[(Me_3Si)_2P]_2PH$; the latter can be lithiated to $[(Me_3Si)_2P]_2PLi$ (*38*). The chemical behavior of these compounds is evident in nonpolar solvents. In ether solutions the completely silylated phosphanes with two or more phosphorus atoms—as well as their derivatives with PH groups—undergo complicated reactions with lithiating agents. These reactions, after $P(SiMe_3)_3$ and $LiP(SiMe_3)_2$ are eliminated, yield phosphorus-rich phosphides, especially Li_3P_7 (*20*).

To investigate such reactions further, various substituted, phosphorus-rich silylphosphanes are needed as starting compounds. The following investigations aim at the preparation of phosphorus functional tri- and tetraphosphanes, in which particular phosphorus atoms with reactive substituents (H, Li, halogen, $SiMe_3$) are built in, while other phosphorus atoms with equally defined positions remain blocked by alkyl groups.

A. REACTION OF PCl_3 WITH $(Me_3C)P(SiMe_3)_2$ AND $MeP(SiMe_3)_2$

The reactions of $(Me_3Si)_3P$ with PCl_3 yielding $(Me_3Si)_2P—PCl_2$ indicate, by cleavage of the Si—P bond, with elimination of Me_3SiCl, and by formation of a new P—P bond, a way to construct functional diphosphanes (*38*). The compounds thus obtained are thermolabile if more Me_3Si-substituted phosphorus atoms are contained in the molecules. The reactions of $(Me_3C)P(SiMe_3)_2$ (**41**) and $MeP(SiMe_3)_2$ (**42**) with PCl_3 occur in an analogous manner (*20*), as shown in Eq. (5) (*39*).

$$\underset{\textbf{(40)}}{PCl_3} + \underset{\textbf{(41)}}{(Me_3C)P(SiMe_3)_2} \xrightarrow[n\text{-pentane}]{-78^\circ C} \underset{\textbf{(43)}}{(Me_3C)(Me_3Si)P—PCl_2} + Me_3SiCl \qquad (5)$$

Similarly, $MeP(SiMe_3)_2$ yields $Me(Me_3Si)P—PCl_2$ (**44**). The reaction given in Eq. (5), when set up in 1:1 molar ratio at −78°C, produces within 24 hours compound **43** almost quantitatively. The colorless reaction mixture remains apparently unchanged. Compound **43** is unstable in solution. Upon warming at 20°C its decomposition occurs with formation of a yellow color.

$MeP(SiMe_3)_2$ (**42**) reacts with PCl_3 according to Eq. (5) substantially faster than compound **41** does. The reaction in pentane at −78°C is already completed after 15 minutes with the formation of $Me(Me_3Si)P—PCl_2$ (**44**). If the concentration of **42** is increased, it can, according to the molar ratio of the reagents, also lead to substitution of the second and third chlorine atoms of PCl_3. Within a few minutes at 20°C **44** decomposes, while the solution takes on an intense yellow color and a yellow, amorphous precipitate is formed.

B. REACTION OF $(Me_3C)(Me_3Si)P—PCl_2$ WITH $LiP(SiMe_3)_2$ AND $LiCMe_3$

The reaction of PCl_3 with **41** in both the molar ratios 1:1 and 1:2 produces **43**. No further elimination of Me_3SiCl occurs between **43** and **41** at −78°C in pentane. If, however, **43** is reacted with the phosphides $LiP(SiMe_3)_2$ or $LiP(SiMe_3)CMe_3$, the triphosphanes **46** and **47**, respectively, are formed according to Eq. (6) (*39*).

$$\mathbf{43} + LiP(SiMe_3)R \longrightarrow (Me_3C)(Me_3Si)P—P(Cl)—P(SiMe_3)R + LiCl \qquad (6)$$

$$[R = SiMe_3\ (\mathbf{46}),\ R = CMe_3\ (\mathbf{47})]$$

In order to carry out the reaction, compound **43** must be brought to −78°C and then a solution of $LiP(SiMe_3)_2 \cdot 2THF$ in toluene must be slowly added. Initially the reaction mixture turns yellow and then, because of the separation of LiCl, becomes cloudy. After 2 hours, compound **43** has completely reacted. The main product is $(Me_3C)(Me_3Si)P—P(Cl)—P(SiMe_3)_2$ (**46**) (about 55 mol%), in addition to which about 10% of $[(Me_3Si)_2P]_2PCl$ (**48**) is formed, as well as 20% $(Me_3Si)_3P$, 10% **41**, and 1% $P_2(SiMe_3)_4$ (**49**). Formation of **48** results from compound **46** by cleavage of the P—P bond by $LiP(SiMe_3)_2$ according to Eq. (7).

$$\underset{(\mathbf{46})}{(Me_3C)(Me_3Si)P—P(Cl)—P(SiMe_3)_2} + \underset{(\mathbf{45})}{LiP(SiMe_3)_2} \xrightarrow[n\text{-pentane}]{-78°C}$$

$$\underset{(\mathbf{48})}{(Me_3Si)_2P—P(Cl)—P(SiMe_3)_2} + \underset{(\mathbf{50})}{LiP(SiMe_3)CMe_3} \qquad (7)$$

This is even more evident if $LiP(SiMe_3)_2$ is used in excess. Compound **50** and $LiP(SiMe_3)_2$ also, to a small extent, finally react with Me_3SiCl to form $(Me_3Si)_3P$ and **41**. Transmetallation reactions, which by means of an Li/Cl exchange between $LiP(SiMe_3)_2$ and **46** or **43** [intermediate formation of $(Me_3Si)_2PCl$ with $LiP(SiMe_3)_2$ and further reactions] yield the diphosphane **49**, play only a secondary role.

If in order to prepare the triphosphane according to Eq. (6), the analogous bromine compound $(Me_3C)(Me_3Si)P—PBr_2$ is used instead of compound **43**, transmetallation dominates and compound **49** becomes the principal product. The symmetric diphosphane $P_2(SiMe_3)_2(CMe_3)_2$ (**52**) [formed just like **49** from **50** according to Eq. (7)], as well as $P_2(SiMe_3)_3(CMe_3)$ (**51**) (cross product of **50** and **45**), can also be detected, $(Me_3Si)_2P1\text{-}P2(Cl)\text{-}P3(SiMe_3)CMe_3$ contains in P2 and P3 two chiral centers and exists in two diastereomeric configurations which occur in a 6:1 ratio. In solution, **46** is stable only at low temperatures. This can be explained by the presence of both Me_3Si and Cl substituents in the same phosphane molecule. At 20°C it decomposes yielding soluble products which are not easily defined.

C. $(Me_3Si)_2P—P(H)—P(SiMe_3)CMe_3$

If the solution of compound **46** obtained according to Eq. (6) is mixed slowly at $-78°C$ with the equivalent amount of $LiCMe_3$ in *n*-pentane, a deepening of the color from yellow to orange is observed. After the reaction mixture is warmed for some hours at 20°C, its color becomes paler. A reaction between $LiCMe_3$ and Me_3SiCl, which according to Eq. (5) is present in the mixture, cannot, under the chosen conditions, be assumed. The principal product of the reaction (with 1:1 molar ratio) is $(Me_3Si)_2P—P(H)—P(SiMe_3)CMe_3$ (**53**). It is formed according to Eq. (8) by transmetallation between **46** and $LiCMe_3$.

$$\mathbf{46} + LiCMe_3 \xrightarrow[n\text{-pentane}]{-78°C} \underset{\mathbf{(54)}}{(Me_3Si)_2P—P(Li)—P(SiMe_3)CMe_3} + Me_3CCl \qquad (8)$$

Formation of the phosphide **54** can be recognized by the orange color in the reaction solution when $LiCMe_3$ is added. Addition of Me_3CCl causes the subsequent hydrogen substitution for lithium in **54**. As LiCl and isobutene are eliminated, the hydrogenated triphosphane **53** is formed [Eq. (9a)].

$$\mathbf{54} \xrightarrow[-LiCl]{+Me_3CCl} \underset{\mathbf{(53)}}{(Me_3Si)_2P—P(H)—P(SiMe_3)CMe_3} + H_2C{=}CMe_2 \qquad (9a)$$

$$\mathbf{54} \xrightarrow[-LiCl]{+Me_3SiCl} \underset{\mathbf{(55)}}{(Me_3Si)_2P—P(SiMe_3)—P(SiMe_3)CMe_3} \qquad (9b)$$

Simultaneously, **54** forms with Me_3SiCl [from the first reaction stage according to Eq. (5)] the silylated triphosphane **55** [Eq. (9b)]. Substitution by a CMe_3 group, which yields $(Me_3Si)_2P—P(CMe_3)—P(SiMe_3)$-$CMe_3$ (**56**), progresses less favorably than silylation of the secondary phosphorus in compounds **54** and **46**, respectively. This is explained by the steric differences between the CMe_3 and the $SiMe_3$ groups.

The triphosphanes $(Me_3Si)_2P—P(H)—P(SiMe_3)_2$ (**57**) and $(Me_3Si)_2P—P(SiMe_3)—P(SiMe_3)_2$ (**58**) are formed from **48** in a manner similar to that in which **53** and **55** are obtained. The main product, **53**, which cannot be separated as a completely pure substance, forms colorless octahedral crystals.

According to the principle stated in Section IV,B,C, by varying the substituents the compounds $[Me_3C)(Me_3Si)P]_2PH$ (**59**), $(Me_3Si)_2P—P(Cl)—P(SiMe_3)Me$ (**60**), $Me(Me_3Si)P—P(Cl)—P(SiMe_3)(CMe_3)$ (**61**), and $[Me(Me_3Si)P]_2PCl$ (**62**) can also be prepared.

D. Preparation and Properties of the Triphosphides $(Me_3Si)_2P—P(Li)—P(SiMe_3)CMe_3$ and $[(Me_3C)(Me_3Si)P]_2PLi$

The phosphides **54** and $[(Me_3C)(Me_3Si)P]_2PLi$ (**63**) can be easily prepared reaction of the derivative hydrogenated on the secondary phosphorus with either *n*- or *t*-butyllithium, as Eq. (10) illustrates.

$$\underset{(\mathbf{53},\ R = SiMe_3;\ \mathbf{59},\ R = CMe_3)}{R(Me_3Si)P—P(H)—P(SiM3_3)CMe_3} + LiBu \longrightarrow \underset{(\mathbf{54},\ R = SiMe_3;\ \mathbf{63},\ R = CMe_3)}{R(Me_3Si)P—P(Li)—P(SiMe_3)CMe_3} + HBu \tag{10}$$

The lithiation shown in Eq. (10) takes places at 20°C in *n*-pentane. Under these conditions, the reactivity of the lithium alkyl is reduced to such an extent that only the most reactive bond in **53** (and in **59**, respectively) is acted upon and therefore the selective exchange of the phosphorus hydrogen with lithium takes place. The phosphides formed can easily be separated and purified because they dissolve with difficulty in nonpolar solvents. Precipitation of these phosphides is, however, incomplete and can fail to occur if the reaction solutions contain significant concentrations of partially alkylated silylphosphanes such as $(Me_3C)P(SiMe_3)_2$ and $MeP(SiMe_3)_2$.

The ether-free phosphides **54** and $[(Me_3C)(Me_3Si)P]_2PLi$ (**63**) are amorphous pale yellow powders which oxidize spontaneously in air with flames. They can be isolated with a yield of 90–95% if, for their preparation according to Eq. (19), the corresponding hydrogenated triphosphanes **53** and **59**, respectively, are employed in pure form.

If **54** is heated to 133°C, and $[(Me_3C)(Me_3Si)P]_2PLi$ to 194°C, they decompose as indicated by a change in the color of the solution.

E. SUMMARY OF THE RESULTS

The above results show that triphosphanes can be prepared by means of a multiple-stage reaction. They can be obtained experimentally with a one-pot reaction. In the above-quoted examples, the P1 phosphorus atoms are contained in $P(SiMe_3)_2$, $P(SiMe_3)CMe_3$, or $P(SiMe_3)Me$ groups, whereas the P2 phosphorus atoms are substituted with Cl, H, Li, $SiMe_3$, or CMe_3. Formation of the triphosphanes takes place according to the following steps:

1. The first step consists of the reaction of PCl_3 with $P(SiMe_3)_2R$- ($R = CMe_3$, Me). This reaction at −78°C, involving the cleavage of Me_3SiCl, yields the diphosphane $R(Me_3Si)P—PCl_2$ almost quantitatively. In the reactions of PCl_3 with the corresponding phosphides $LiP(SiMe_3)R$ instead of $P(SiMe_3)_2R$, it is not possible to interrupt the reaction at the diphosphane stage. Quite independently from the initial molar ratios, the second chlorine atom in PCl_3 is also substituted, and the triphosphanes $[R(SiMe_3)P]_2PCl$ are formed.
2. The second reaction step requires the use of reactive phosphides:

$$R(Me_3Si)P—PCl_2 + LiP(SiMe_3)R' \longrightarrow R(Me_3Si)P—P(Cl)—P(SiMe_3)R'$$
$$(R = CMe_3, Me;\ R' = SiMe_3, CMe_3, Me)$$

The main products under all variations of R and R′ are the P2-chlorinated triphosphanes. Side reactions such as $SiMe_3/Cl$ exchange, P—P cleavage by $LiP(SiMe_3)R'$, or transmetallations take place only to a small extent. $MeP(SiMe_3)_2$ is an exception inasmuch as it reacts with P-chlorinated phosphanes to yield tri- and even tetraphosphanes.

3. Because of their thermolability (elimination of Me_3SiCl), the P-chlorinated silylphosphanes were reacted with $LiCMe_3$ immediately after their formation at −78°C to yield stable derivatives. In this third reaction step, the following reactions are possible: (A) *tert*-butyl substitution as LiCl is cleaved off; (B) transmetallation yielding phosphides and Me_3CCl: further reactions of the phosphides with Me_3CCl yield P-hydrogenated compounds as isobutene and LiCl are eliminated, and further reactions of the phosphides with Me_3SiCl [from$=$PCl + $P(SiMe_3)_2R$ as before] lead to the P2-silylated triphosphanes.

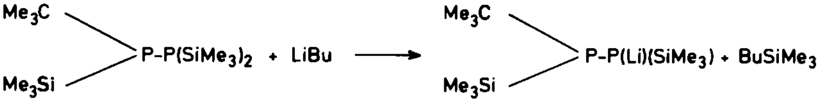
Substitution of Cl in $R(Me_3Si)P1—P2(Cl)—P3(SiMe_3)R'$ with the CMe_3 group occurs as the principal reaction only when $R = R' = Me$. Under all other variations of R and R′ the proportion of P2-*t*-butylated compounds remains under 10%. Obviously, for steric reasons, transmetallation between chlorinated triphosphanes and $LiCM_3$ at −78°C is favored (yield 50–60%). The triphosphides formed are nevertheless only intermediate products, which react further with Me_3CCl as well as with Me_3SiCl as the mixture is warmed to room temperature. Two possible complementary parallel reactions occur. With an increasing number of sterically significant substituents R and R′ (Me < $SiMe_3$ < CMe_3) in the molecule, H-substitution on P2 (according to Step 3B above) becomes favored relative to silylation as the following comparison shows:

$R(Me_3Si)P1—P2(X)—P3(SiMe_3)R'$		Yield ratio of the triphosphanes with:	
R	R′	X = H	X = $SiMe_3$
$SiMe_3$	CMe_3	3.5	1
Me	CMe_3	1.7	1
Me	$SiMe_3$	0.7	1

In all the reactions investigated, product mixtures are formed which are subjected to a thorough fractionating sublimation. Among the series of compounds $R(Me_3Si)P—P(X)—P(SiMe_3)R'$ formed, the hydrogenated triphosphanes (X = H) can be separated by this means. The products are, if R, R′ = $SiMe_3$, **57**; if R = $SiMe_3$, R′ = CMe_3, **53**; and if R, R′ = CMe_3, **59**. The corresponding silylated derivatives (X = $SiMe_3$) cannot be sublimed; they remain in the residue and undergo thermal decomposition as they reach 60–80°C. With the remaining variations of the substituents R, R′ = $SiMe_3$, CMe_3, Me, the corresponding triphosphanes with X = H, $SiMe_3$, CMe_3 can only be enriched in certain sublimed fractions. Lithiation of the hydrogenated triphosphanes **57**, **53**, and **59** is achieved with LiBu almost completely. The resulting phosphides, $[(Me_3Si)_2P]_2PLi$ (**64**), **54**, and **63**, render possible the preparation of further derivatives (X = $SiMe_3$, alkyl, etc.). Furthermore, their reactions in polar ethers are certainly very interesting. interesting.

V. Synthesis of Silylated Tri- and Tetraphosphanes via Lithiated Diphosphanes, and Their Reactions

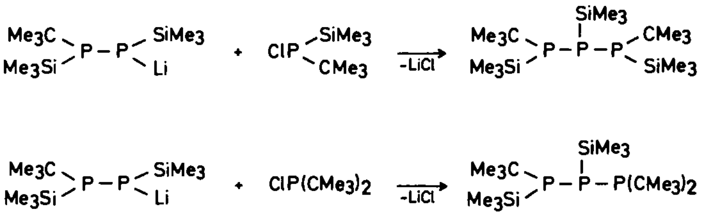
Synthesis of triphosphanes by Si—P bond cleavage with PCl_3 and further reaction of the triphosphane formed with $LiP(SiMe_3)_2$ is described in Section IV. Starting with the lithium derivative of a suitably substituted diphosphane and linking it to the phosphorus atom of a group with the desired substituents is a method which offered itself for the synthesis of partially silylated and alkylated triphosphanes. A possible route to this synthesis was indicated by the observation that the introduction of one Me_3C group in the silylated diphosphane was enough to obtain a lithiated compound stable in ether (*40*), as shown in the following equation:



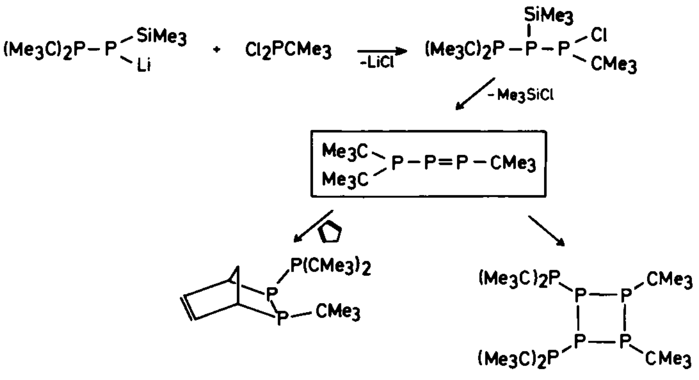
$$(Me_3C)(Me_3Si)P{-}P(SiMe_3)_2 + LiBu \longrightarrow (Me_3C)(Me_3Si)P{-}P(Li)(SiMe_3) + BuSiMe_3$$

Scheme 8 gives a further possible variation in the synthesis of functional triphosphanes (*40*).

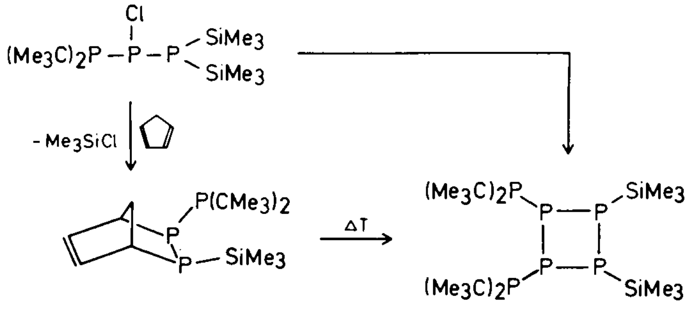
Schemes 9 and 10 show the synthesis of triphosphanes with functional substituents in the 1,2-position. Additional reaction proceeds with elimination of Me_3SiCl and the formation of the corresponding cyclotetraphosphane in which the $P(CMe_3)_2$ groups are adjacent. The reaction progresses with the formation of the P=P double bond, which can be proved by the addition of cyclopentadiene (Scheme 10). The



SCHEME 8



SCHEME 9

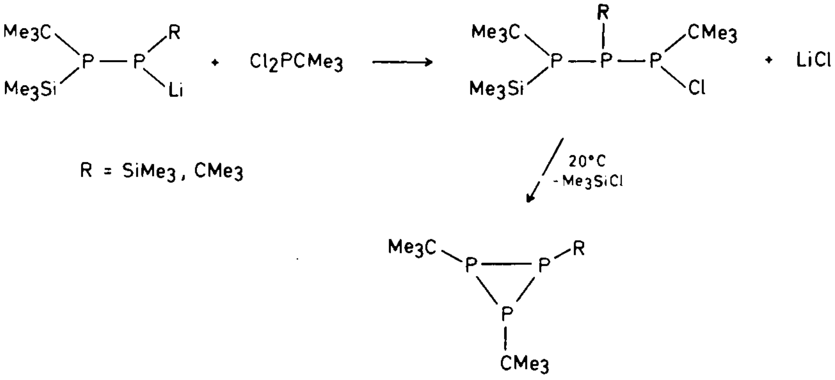


SCHEME 10

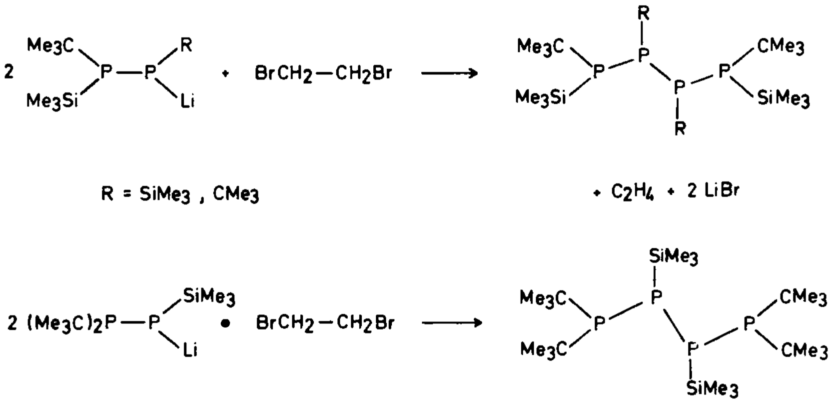
functional groups can also be placed in the 1,3-position of the tetraphosphane, as illustrated by Scheme 11.

The tetraphosphane synthesis developed from the observation by Schumann *et al.* (41) of the formation of $P_2(SiMe_3)_4$ in the reaction of $LiP(SiMe_3)_2$ with $BrH_2C—CH_2Br$. The reactions proceed according to Scheme 12.

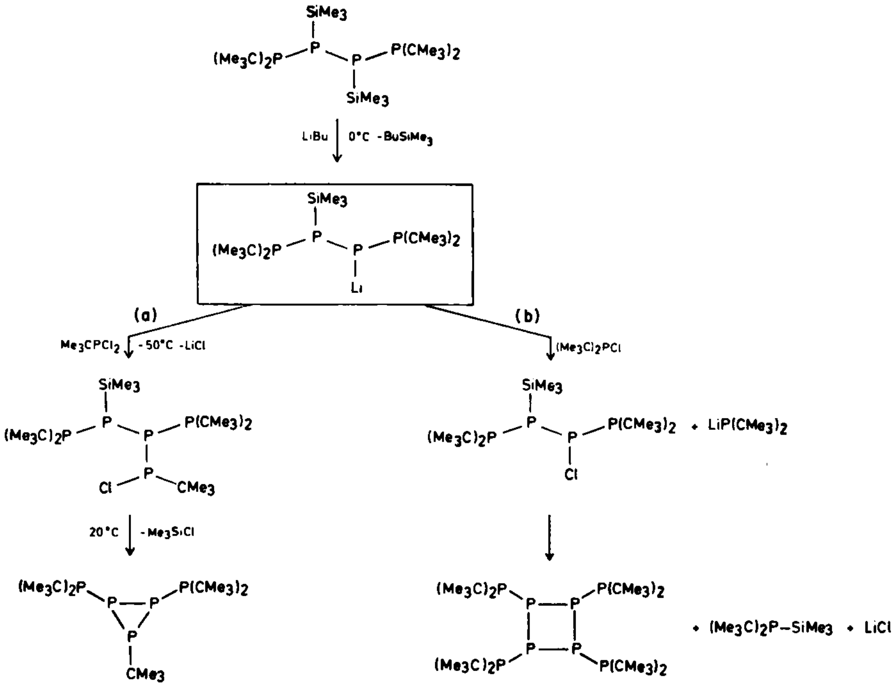
Scheme 13 illustrates the many reaction possibilities which these compounds exhibit. In Scheme 13a, the reaction of the lithium phosphide with Me_3CPCl_2 results in the formation of the cyclotriphosphane after the elimination of Me_3SiCl from positions 1 and 3. On the other hand, according to Scheme 13b, in the reaction with $(Me_3C)_2PCl$, the lithium phosphide undergoes a lithium exchange reaction. The elimination of Me_3SiCl from the adjacent phosphorus atoms follows; thus the cyclotetraphosphane $P_4[P(CMe_3)_2]_4$ is formed. The resulting Me_3SiCl reacts with $LiP(CMe_3)_2$ (formed by transmetallation) to yield $(Me_3C)_2P—SiMe_3$.



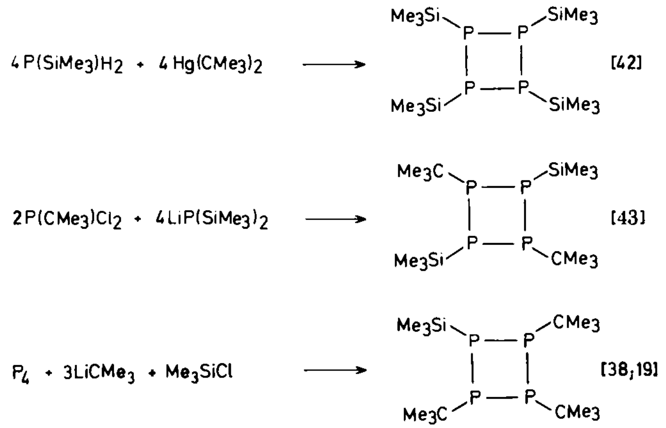
SCHEME 11



SCHEME 12



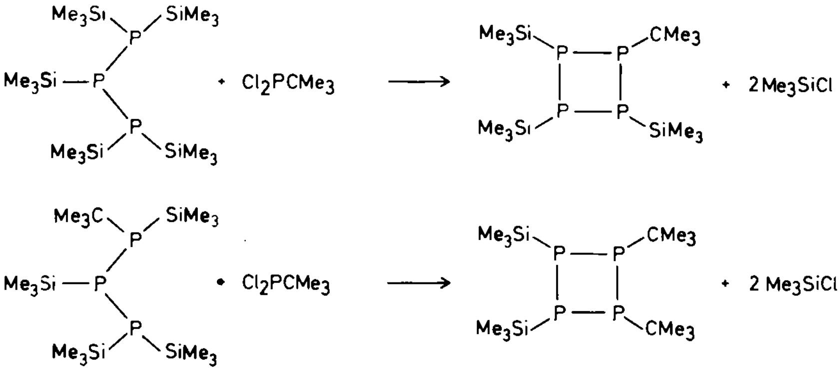
SCHEME 13



SCHEME 14

VI. Silylated Cyclotetraphosphanes

Within the research concerned with the lithiation of silylated, phosphorus-rich phosphanes in ethers, the corresponding cyclotetraphosphanes constitute an interesting group. Those already described in the literature are given in Scheme 14 along with their formation reactions. The missing compounds in this series [i.e., *cis*-$P_4(CMe_3)_2(SiMe_3)_2$ and $P_4(CMe_3)(SiMe_3)_3$] can be prepared with the aid of the synthesis of the appropriate substituted triphosphanes by eliminating Me_3SiCl, according to Scheme 15. cis-$P_4(CMe_3)_2(SiMe_3)_2$ forms pale yellow crystals of melting point 116°C; $P_4(CMe_3)(SiMe_3)_3$ forms yellow crystals of melting point 143 ± 2°C.



SCHEME 15

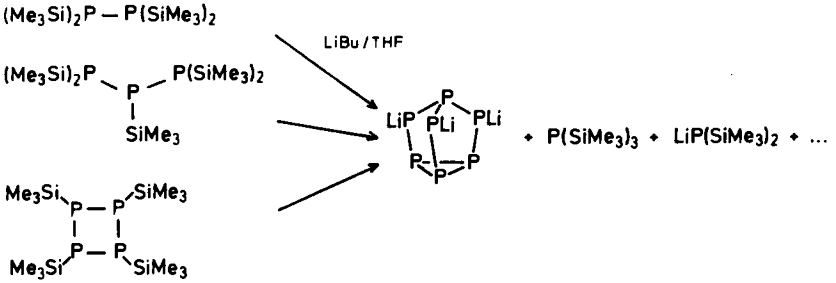
VII. Reactions of Silylated Triphosphanes and Cyclotetraphosphanes with Lithium Alkyls

It is known from the preceding research that phosphorus-rich silylphosphanes or their related lithium phosphides undergo, with LiBu in ether, reactions in which a structural transformation occurs, as shown in Scheme 16 (*20*). The reactions of the partially silylated tri- and cyclotetraphosphanes were explored in order to come closer to understanding the above reactions. It can be taken for granted that the P—C bond is not affected in such reactions.

A. REACTIONS OF LITHIUM PHOSPHIDES $(Me_3Si)_2P—P(Li)—P(SiMe_3)(CMe_3)$ AND $[(Me_3C)(Me_3Si)P]_2PLi$ IN ETHERS

1. *The Reactions of* $(Me_3Si)_2P—P(Li)—P(SiMe_3)(CMe_3)$ (**54**)

Ether solutions of **54** at −15°C slowly take on an orange color. Over the course of some hours the color becomes deeper, turning wine-red. A day later this intense color becomes paler again and what results is a homogeneous orange-red solution. A steady state is nevertheless reached only after 3–4 days (23°C). These solutions have at this point the same composition as the samples kept for 6 hours at 70°C. The products of the reaction of **54** are the four-membered ring $P_4(CMe_3)_3SiMe_3$(**65**)(*38, 39*) along with $LiP(SiMe_3)_2$ and $(Me_3Si)_3P$. The compounds Li_3P_7(**66**)(*45*) and $Li_2P_7CMe_3$(**67**)(*19, 46*) are formed only in modest amounts, as are the partially alkylated compounds such as $(Me_3C)P(SiMe_3)_2$(**41**), $HP(SiMe_3)CMe_3$(**68**), and $Me_3C(Me_3Si)P—P(SiMe_3)Li$(**69**). There exists in other words a parallel between this and the product spectrum of the lithiation of *trans*-$P_4(CMe_3)_2(SiMe_3)_2$(**71**). Of major (*40, 47*) significance for the understanding of the development

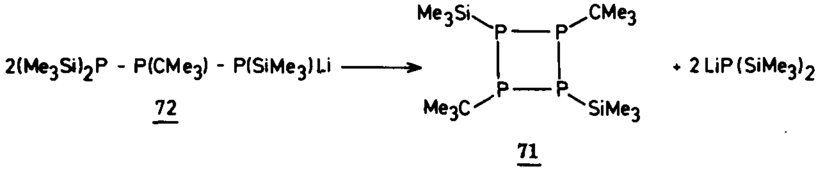


SCHEME 16

of the reaction is the formation of the phosphide $(Me_3Si)_2P$—$P(CMe_3)$—$P(SiMe_3)Li$(**72**). This compound, in the early phases of the reaction of $(Me_3Si)_2P$—$P(Li)$—$P(SiMe_3)CMe_3$(**54**), is the first intermediate product which can be detected. This transition from P2 (**54**) to P1 phosphide (**72**) cannot occur by a peripheral exchange of substituents, because under the chosen conditions the P—C bonds are totally inert. Indeed this transition is a sign that the structural rearrangement of the P—P skeleton is already initiated. In the formation of **72** it must be assumed that several intermolecular complex dismutation steps of the P-chain of **54** occur because equimolar amounts of $LiP(SiMe_3)_2$, **68**, and $Li(Me_3Si)P$—$P(SiMe_3)CMe_3$(**73**) are formed, as well as double the amount of $(Me_3Si)_3P$ and traces of $Li(Me_3Si)P$—$P(SiMe_3)_2$(**74**). This implies also the formation of linear-chain tetra- or pentaphosphides. These substances are however unstable under the reaction conditions (−15°C, THF) (*44*). They undergo further reactions and thus escape detection by NMR. ^{31}P-NMR examination of the product mixture of the reaction of **54** (after **72** has been formed) yields, at this point in the reaction (homogeneous solution, 4 hours, −15°C), the following proportions for the demonstrable atoms and groups: $Li:P:SiMe_3:CMe_3 = 3:9:14:3$. If one compares these values with the triplicated formula of the starting compound **54**, that is $Li_3P_9(SiMe_3)_9(CMe_3)_3$, it is found that the quota of $SiMe_3$ groups in the reaction products is too high. This can be explained by the fact that in the initial homogeneous solution, phosphorus-rich compounds are already present which cannot be detected by ^{31}P-NMR measurements; their signals in the spectrum are masked by the background noise. Their existence can, however, be seen at a more advanced stage of the reaction by a broad unresolved "signal peak," whose chemical shift (80–20 ppm) indicates that unstrained phosphorus five-membered rings probably exist as integral structural elements. Accordingly, in the initial phase of this reaction, through repeated connections of small phosphide units, construction of phosphorus frameworks of higher order is already taking place. At the same time elimination of small molecules and transfer of the silyl substituents to molecules such as $LiP(SiMe_3)_2$ and $(Me_3Si)_3P$ occurs, a fact clearly expressed by the observed concentration ratios of the various groups.

An example of the formation of a ring and of the "desilylation" is given by the formation of *trans*-$P_4(CMe_3)_2(SiMe_3)_2$(**71**) according to Eq. (11), demonstrated, with maximal concentration of compound **72**, after 10 hours at −15°C. Closure of the ring to form **71** occurs after $LiP(SiMe_3)_2$ is eliminated, presumably in a two-stage reaction through the *n*-pentaphosphide $Li(Me_3Si)P$—$P(CMe_3)$—$P(SiMe_3)$—$P(CMe_3)$—

$P(SiMe_3)_2$, an hypothesized intermediate product which has not yet been detected.



(11)

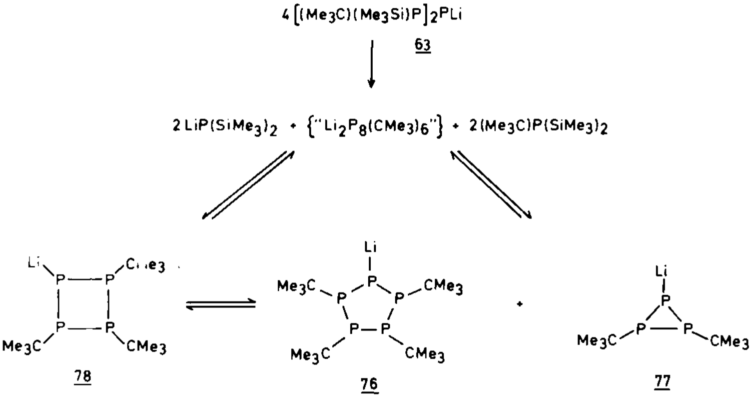
Formation of **71** is accompanied by metallation by $LiP(SiMe_3)_2$ while $(Me_3Si)_3P$ is eliminated. This means that the further course of the reaction proceeds by the rearrangement of *trans*-$LiP_4(CMe_3)_2SiMe_3$(**70**). The reaction sequence shown raises the P:$SiMe_3$ ratio from the original 1:1 in **72** or **54** to 4:1 in **70**. Due to their property of being excellent leaving groups, the $SiMe_3$ groups are "concentrated" in small molecules such as $LiP(SiMe_3)_2$ and $(Me_3Si)_3P$, thus causing the formation of new P—P bonds. In the further course of the reaction the P_4 ring of **70** reopens and secondary reactions follow, again with the formation of $LiP(SiMe_3)_2$ and $(Me_3Si)_3P$. The desilylation products are perceived in the ^{31}P-NMR spectrum only by a rather characteristic broad signal peak between 80 and 20 ppm, so that no more information can be obtained about the constitution of the products formed. In this phase of the reaction (3 hours, 23°C) formation of $P_4(CMe_3)_3SiMe_3$ **65** also begins. Once the final stage of the reaction of **54**, after 3 days (23°C), is reached, the proportion of **65** is significantly increased. Coincidently, with a decrease in the intensity of the signal peak the phosphides Li_3P_7(**66**) and $Li_2P_7CMe_3$(**67**) can also be detected. The compounds **65**, **66**, and **67** are probably the degradation products of hitherto unknown higher phosphides (*39*).

2. *Reactions of* $[(Me_3C)(Me_3Si)P]_2PLi$ (**63**)

Solutions of **63** in THF or DME are stable at 23°C for a few hours. The structure rearranges under these conditions with a half-life of approximately 26 days. For **54**, the half-life at −15°C THF is about 6 hours. Without any externally recognizable alteration of the yellow solution of **63**, after a few days, $LiP(SiMe_3)_2$ and $(Me_3C)P(SiMe_3)_2$(**41**) can be observed as initial products in the ^{31}P-NMR spectrum of the solution. These compounds are also formed in the further course of the reaction, always in the same amount. After 60 days (23°C/DME) the solution shows the following composition (values in mol% phosphorus from the integration of the ^{31}P-NMR spectrum): **63**, 14%; $LiP(SiMe_3)_2$ (**45**), 26%; **41**, 26%; $LiP_5(CMe_3)_4$(**76**), 19%; $LiP_3(CMe_3)_2$(**77**), 5%; $LiP_4(CMe_3)_3$(**78**), 2%; **69**, 3%; unknown compounds, 5%.

A balance of all the products formed yields the ratio: $Li:P:SiMe_3:CMe_3 = 1:3.2:2:2.2$, which, taking into account the accuracy of the measurements is in agreement with the group ratio of the initial compound **69** (39). Accordingly, reaction of **63** yields only "small, defined molecules," whose constitution and relative proportions are easily determined by the ^{31}P-NMR spectra. From the overall equation for the reaction (Scheme 17), the formation of the main products found, $LiP(SiMe_3)_2$, $(Me_3C)P(SiMe_3)_2$(**41**), **76**, **77**, and **78**, can only be qualitatively understood.

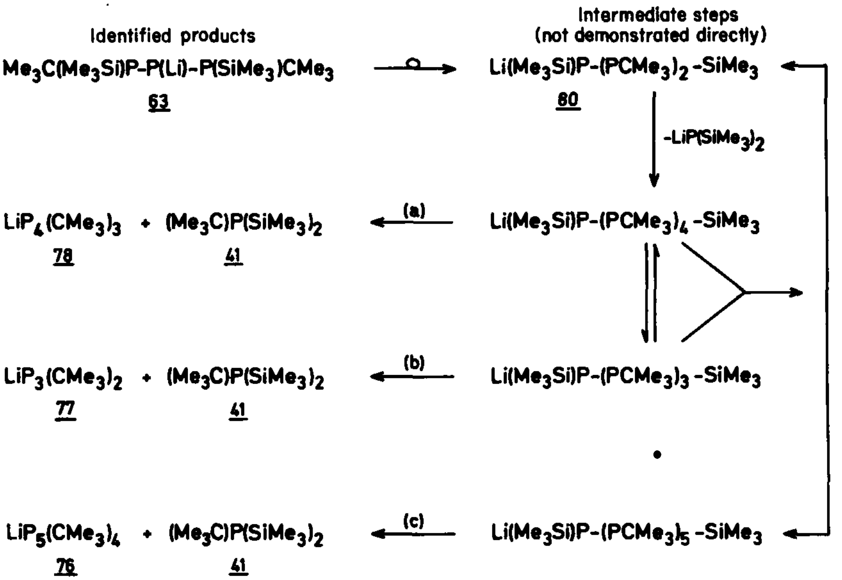
As a result, compounds **76** and **77** should be formed in equal proportions. The experimental results differ from this inasmuch as **76** is preferentially formed. This can be explained by the following considerations. It has been shown independently in earlier investigations that the dismutation of **78**, yielding **76** and **77**, is possible in THF. This takes place in the presence of a base [LiBu, $LiP(SiMe_3)_2$] even at 0°C. It must be supposed that as precursors of the cyclic phosphides **76**, **77**, and **78** there exist unbranched phosphide chains, whose cyclization with parallel elimination of $(Me_3C)P(SiMe_3)_2$ yields phosphorus rings of various size according to the length of the chain. The validity of such an assumption is indicated by comparing it to the reaction of *cis*-$P_4(CMe_3)_2(SiMe_3)_2$(**79**) with LiR (R = Me, Bu) in THF (*44*) (Section VII,B). In that case the first step of the reaction consists exclusively of the opening of the ring of **79**. The resulting *n*-tetraphosphides $Me_3C(Me_3Si)P—P(CMe_3)—P(Li)—P(SiMe_3)R$ and $Li(Me_3Si)P—P(CMe_3)—P(CMe_3)—P(SiMe_3)R$ are unstable in THF. Above −30°C



SCHEME 17

they undergo a structural rearrangement which yields among other products **76** and **77**. The analogy with the behavior of **63** becomes evident, if as first reaction step a rearrangement yielding the primary phosphide Li(Me_3Si)P—P(CMe_3)—P($SiMe_3$)CMe_3(**80**) is postulated, as was observed for the more highly silylated homologues **54** and **64**. An NMR spectroscopic proof of formation of **80** and of further intermediates is not possible at the temperature required for the reaction to take place (23°C), because the secondary reactions proceed faster than the primary step. By elimination of LiP$(SiMe_3)_2$, linear-chain higher phosphides can be constructed from **80**. These can nevertheless not be lengthened to any desired extent. Their decreasing stability as their size increases is manifested by dismutations; in these the chain lengths are altered by breaking and reforming P—P bonds in an intermolecular reaction (*48–54*). The only possibility to stabilize the unbranched phosphides remains ring closure as smaller molecules like **41** or LiP$(SiMe_3)_2$ are split off. Ramifications, which can likewise stabilize larger phosphorus structures, can develop only if secondary phosphorus atoms are also substituted in a chain by means of functional groups (rearrangement of **74**, **64**, or **54**).

These considerations permit the compilation of Scheme 18, which summarizes the rearrangement of **63**.



SCHEME 18

The reactions given in Scheme 18 provide a satisfying explanation for the formation of all the observed products and their relative proportions. The observed preferred tendency toward formation of **76** can also be explained. The stability of linear-chain phosphanes is significantly increased by substitution with bulky *tert*-butyl groups. Thus $(PCMe_3)_4(SiMe_3)_2$ (*50*) or $(PCMe_3)_4H_2$ (*50*) can be heated above 60°C without decomposing, while the phenyl compounds $(PC_6H_5)_4(SiMe_3)_2$ and $(PC_6H_5)_4H_2$ (*49*) decompose rapidly even at room temperature. It is therefore plausible that the *tert*-butyl substitution of adjacent phosphorus atoms stabilizes the dismutation of **80** as far as the *n*-hexaphosphide $LiP_6(CMe_3)_5(SiMe_3)_2$, before cyclization to the pentaphosphide **76** occurs (reaction c, Scheme 18). Formation of **77** according to step (b) and that of **78** according to step (a) are consequently only collateral branches of the main reaction. Comparison of the reactions of the compounds $(Me_3Si)_2P{-}P(Li){-}P(SiMe_3)_2$, $(Me_3Si)_2P{-}P(Li){-}P(CMe_3)(SiMe_3)$, and $[(Me_3C)(Me_3Si)P]_2PLi$ clearly shows the influence of the Me_3C groups upon the course of the reactions.

B. *Reactions of Silylated Cyclotetraphosphanes with Lithium Alkyls*

Phosphorus–silicon bonds in trimethylsilyl phosphanes can be cleaved by lithium alkyls (*11*). Such reactions occur in most cases even below 20°C in the presence of a solvating ether like THF or DME.

$$=P{-}SiMe_3 + LiR \longrightarrow LiP{=} + RSiMe_3 \qquad (12)$$

In the series of silylated cyclotetraphosphanes $P_4(CMe_3)_n(SiMe_3)_{4-n}$, ($n = 0-3$), the behavior of $P_4(CMe_3)_3SiMe_3$ (**65**) and *trans*-$P_4(CMe_3)_2(SiMe_3)_2$ (**71**) toward lithium alkyls [LiMe, Li(n – Bu)] was investigated earlier (*47*). Both compounds react according to Eq. (12). Whereas the phosphide $LiP_4(CMe_3)_3$ (**81**) formed from **65** can be obtained as a crystalline THF adduct, *trans*-$LiP_4(CMe_3)_2SiMe_3$ (**70**) could not be isolated in the past (*40*), because secondary reactions which alter the phosphorus structure of **70** take place during the course of its formation from **71**. Compound **70** yields the following products: the cyclotetraphosphane **65** and $R'P(SiMe_3)_2$ (R' = Li, $SiMe_3$, CMe_3, Me, or *n*-Bu), as well as phosphorus-rich unidentified compounds. The formation of the P_7 framework is only observed in the form of $Li_2P_7CMe_3$ and $LiP_7(CMe_3)_2$, and then only to a small extent (<5%).

The reactive behavior of $P_4(SiMe_3)_4$ (**85**) with respect to lithium alkyls was also the object of former investigations (*47*). It is these that firmly established the formation of Li_3P_7, $P(SiMe_3)_3$, and $LiP(SiMe_3)_2$.

1. *Reactions of* $P_4(SiMe_3)_4$ *with Lithium Alkyls*

The reactions of **85** with LiR (R = Me, *n*-Bu) in stoichiometric quantities are completed within a few minutes in THF at a temperature between −60 and −50°C. These reactions do not yield the initially expected $LiP_4(SiMe_3)_3$; instead, the secondary phosphide $(Me_3Si)_2P—P(SiMe_3)—P(Li)—P(SiMe_3)R$ is formed almost exclusively. The latter is not the primary product of ring opening. By altering the solvent polarity, the first-formed product can be obtained. If the reaction of **85** with LiR is performed in a solvent mixture in which Et_2O:THF = 14:1, at a temperature of between −50 and −40°C, after 30 minutes reaction time the formation of the expected primary *n*-tetraphosphide can be demonstrated (*44*) [Eq. (13)].

$$\underset{(\mathbf{85})}{P_4(SiMe_3)_4} + LiR \longrightarrow \underset{(R = Me, \mathbf{86};\ R = n\text{-Bu}, \mathbf{87})}{Li(PSiMe_3)_4R} \qquad (13)$$

In pure Et_2O (without added THF) the reaction times are considerably lengthened. Accordingly, in the first reaction step, a P—P bond of **85** is cleaved by the nucleophilic attacking lithium alkyl. Because of the symmetrical structure of **85** only one primary product can be yielded by the opening of its four-membered ring. When cooled THF is added to this solution of compound **86**, or of **87**, rapid isomerization to the P2 *n*-tetraphosphide follows, as illustrated by Eq. (14).

$$\underset{(R = Me, \mathbf{86};\ R = n\text{-Bu}, \mathbf{87})}{Li(PSiMe_3)_4R} \xrightarrow{THF} \underset{(R = Me, \mathbf{88};\ R = n\text{-Bu}, \mathbf{89})}{(Me_3Si)_2P—P(SiMe_3)—P(Li)—P(SiMe_3)R} \qquad (14)$$

The isomerization according to Eq. (14) is in contrast with the behavior of the secondary triphosphides $(Me_3Si)_2P—P(Li)—P(SiMe_3)R$ (R = $SiMe_3$, CMe_3). These compounds under similar conditions yield the primary phosphides $(Me_3Si)_2P—P(R)—P(SiMe_3)Li$, whose formation is nevertheless linked with further reactions which change the P framework (*20*). On the other hand, the 1,3-displacement shown in Eq. (14) between lithium and a functional $SiMe_3$ group takes place quantitatively without the formation of further products. The orange-yellow solutions of the silylated *n*-tetraphosphides in THF are stable for several hours at −78°C. They decompose between −30 and −20°C within a few minutes and at room temperature within seconds with the appearance of a deep red color.

The ^{31}P-NMR spectra of the homogeneous solutions in this phase of the reaction show only the formation of $(Me_3Si)_3P$ and $LiP(SiMe_3)_2$, as well as small quantities of $RP(SiMe_3)_2$ (R = Me, *n*-Bu); information about the fate of the remaining phosphorus is lost in the background noise. Further changes in the composition of the solutions take place only slowly. In accordance with previous investigations (*47*), at 20°C the formation of Li_3P_7 can be demonstrated only after several days. Numerous resonance signals of weaker intensity indicate that in the final stage of the reaction of silylated *n*-tetraphosphides, along with the products mentioned, other phosphorus-rich compounds are also formed, whose identification has not yet been possible (*44*).

a. Preparation and Properties of the n-Tetraphosphanes Formed from $P_4(SiMe_3)_4$. The thermolabile *n*-tetraphosphides obtained from **85** and LiMe or Li(*n*-Bu) have been detected only through their ^{31}P-NMR spectra. These compounds yield with Me_3SiCl or MeCl the stable *n*-tetraphosphanes whose isolation is possible. Thus the results given in Section VII,B,1 are further confirmed. The changes shown in Eqs. (15)–(17) proceed without side reactions at low temperatures with sufficient speed so that, in comparison to them, the structural modifications of the *n*-tetraphosphide are negligible (*44*).

For its transformation into the corresponding silyl derivative, the orange-yellow solution of the *n*-tetraphosphide **88**, immediately after its formation from **85** (with LiMe in THF, −50°C), is reacted with Me_3SiCl. The reaction's progress, described in Eq. (15), can be recognized by a change in color to pale yellow.

$$\underset{\textbf{(88)}}{(Me_3Si)_2P\text{—}P(SiMe_3)\text{—}P(Li)\text{—}P(SiMe_3)Me} \xrightarrow[-LiCl]{+Me_3SiCl} \underset{\textbf{(90)}}{Me_3Si(PSiMe_3)_4Me} \qquad (15)$$

After slow warming to 20°C, a clear colorless solution finally results, whose ^{31}P-NMR spectrum indicates nearly complete formation of **90**. In the following work-up, compound **90** can be isolated as colorless needle-shaped crystals. As its melting point is reached (about 49°C), it degrades slowly, manifested by a turning of the color to yellow. At this point, formation of $MeP(SiMe_3)_2$ can be demonstrated. Formation of **90** according to Eq. (15) indirectly proves that the reaction of the cyclotetraphosphane **85** with LiMe yields an open-chain *n*-tetraphosphide; the position occupied by lithium is nevertheless not yet determined. In order to reach a definite conclusion about this, the phosphide **89**, obtained in a further reaction of **85** with Li(*n*-Bu) (THF/−50°C), was transformed into the methyl derivative **91** by MeCl, as indicated in Eq. (16).

$$\mathrm{(Me_3Si)_2P{-}P(SiMe_3){-}P(Li){-}P(SiMe_3)Bu + MeCl} \longrightarrow$$

(89)

$$\mathrm{(Me_3Si)_2P{-}P(SiMe_3){-}P(Me){-}P(SiMe_3)Bu + LiCl} \tag{16}$$

(91)

The formation of **91** shown in Eq. (16) is also manifested by the gradually paler color of the orange-yellow solution of **89**.

As further proof of the course of the reaction between **85** and lithium alkyls, the primary product **86**, resulting from the opening of the ring in compound **85** according to Eq. (13), was reacted anew with MeCl (*44*). At $-40°\mathrm{C}$, formation of the symmetrical *n*-tetraphosphane **92** takes place, as shown in Eq. (17). This is an equally stable derivative, whose $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectrum shows the characteristic resonances of an AA′XX′ spin system.

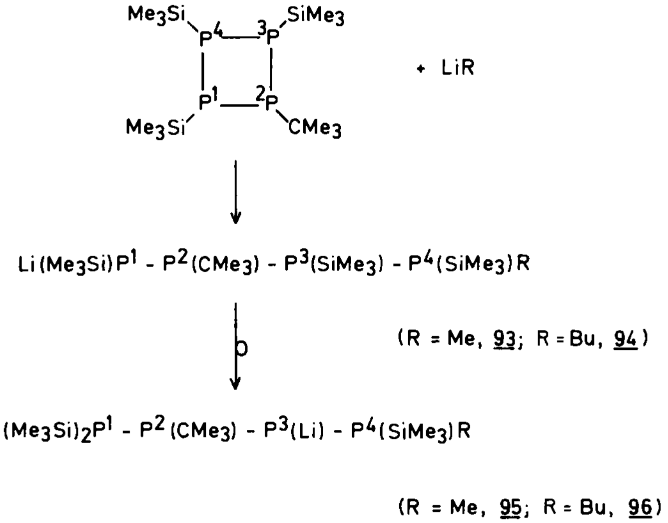
$$\mathrm{Li(PSiMe_3)_4Me + MeCl} \longrightarrow \mathrm{Me(PSiMe_3)_4Me + LiCl} \tag{17}$$

(86) **(92)**

2. *Reactions of* $\mathrm{P_4(SiMe_3)_3CMe_3}$ *with Lithium Alkyls*

Reactions of $\mathrm{P_4(SiMe_3)_3CMe_3}$ with LiR (R = Me, *n*-Bu) have been conducted under the same conditions as were the reactions of $\mathrm{P_4(SiMe_3)_4}$ given in Section VII,B,1. The cyclophosphane reacts completely with LiR at $-45°\mathrm{C}$ in THF or DME within a few minutes, whereas in nonpolar hydrocarbons no reaction is observed after weeks even at 20°C. The reaction consists of the opening of the ring in $\mathrm{P_4(SiMe_3)_3CMe_3}$ by P—P bond cleavage, as shown in Scheme 19; linear-chain *n*-tetraphosphides are formed (*44*).

The lithium alkyl attacks as a nucleophile the P4 atom of $\mathrm{P_4(CMe_3)(SiMe_3)_3}$, so that its bond with P1 or P3 is cleaved. In both cases, the same compounds are formed. The reactions of $\mathrm{P_4(CMe_3)(SiMe_3)_3}$ with LiR yield in THF nearly quantitatively the secondary *n*-tetraphosphides **95** and **96**. Moreover, the primary *n*-tetraphosphides **93** and **94** occur only as intermediate products and they cannot be detected by $^{31}\mathrm{P}$-NMR spectroscopy. Their identification can nevertheless be achieved if instead of pure THF a 9:1 $\mathrm{Et_2O}$:THF solvent mixture is employed. As more THF is added at -50 to $-40°\mathrm{C}$ to a solution of **93** or **94**, isomerization into the secondary *n*-tetraphosphides **95** or **96**, respectively, is accomplished by means of a 1,3-displacement between lithium and an $\mathrm{SiMe_3}$ group. The reaction pathway given is thus confirmed.



SCHEME 19

The *n*-tetraphosphides formed according to Scheme 19 are stable for some hours at −40°C in the presence of THF. As these orange-yellow solutions are brought to room temperature a quick decomposition takes place; thereafter the formation of $LiP(SiMe_3)_2$, $(Me_3Si)_3P$, and minor quantities of $RP(SiMe_3)_2$ (R = Me, *n*-Bu) can be demonstrated. Further compounds cannot be observed even after the reaction solution is allowed to stand several days. After 10–20 hours heating of the NMR samples at 70°C, traces of Li_3P_7 and of $Li_2P_7CMe_3$ can be detected. The ^{31}P-NMR spectra measurements of relatively concentrated solutions indicate, with the appropriate amplification, that the bulk of the effective products of the decomposition is concealed in a noncharacteristic broad "signal peak" between +100 and 140 ppm. Further identification of these products by this method is not feasible.

a. Preparation and Properties of the n-Tetraphosphanes from $P_4(SiMe_3)_3CMe_3$. The thermolabile *n*-tetraphosphides obtained from the reactions of $P_4(SiMe_3)_3(Me_3)$ with lithium alkyls have been transformed with Me_3SiCl or MeCl into more stable *n*-tetraphosphanes (*44*). The reactions illustrated in Eq. (18) proceed quickly and without side reactions at about −40°C. They generate with high yields the corresponding silyl or methyl derivatives of the phosphides.

It was furthermore possible to prove that, as expected, during the silylation of primary and of secondary *n*-tetraphosphides, as Eqs. (18b) and (18c) indicate, the same products are formed. The extraordinarily

$$\mathrm{(Me_3Si)_2P{-}P(CMe_3){-}P(Me){-}P(SiMe_3)R} \qquad \mathrm{R = Me, (}n\mathrm{\text{-}Bu)} \qquad (18a)$$

97 (**98**)

$$\Big\uparrow {\scriptstyle \mathrm{+MeCl} \atop \scriptstyle \mathrm{-LiCl}}$$

$$\mathrm{(Me_3Si)_2P{-}P(CMe_3){-}P(Li){-}P(SiMe_3)R} \qquad (18b)$$

95 (**96**)

$$\Big\downarrow {\scriptstyle \mathrm{+Me_3SiCl} \atop \scriptstyle \mathrm{-LiCl}}$$

$$\mathrm{(Me_3Si)_2P{-}P(CMe_3){-}P(SiMe_3){-}P(SiMe_3)R} \qquad (18c)$$

99 (**100**)

$$\Big\uparrow {\scriptstyle \mathrm{+Me_3SiCl} \atop \scriptstyle \mathrm{-LiCl}}$$

$$\mathrm{Li(Me_3Si)P{-}P(CMe_3){-}P(SiMe_3){-}P(SiMe_3)R} \qquad (18d)$$

93 (**94**)

$$\Big\downarrow {\scriptstyle \mathrm{+MeCl} \atop \scriptstyle \mathrm{-LiCl}}$$

$$\mathrm{Me(Me_3Si)P{-}P(CMe_3){-}P(SiMe_3){-}P(SiMe_3)R}$$

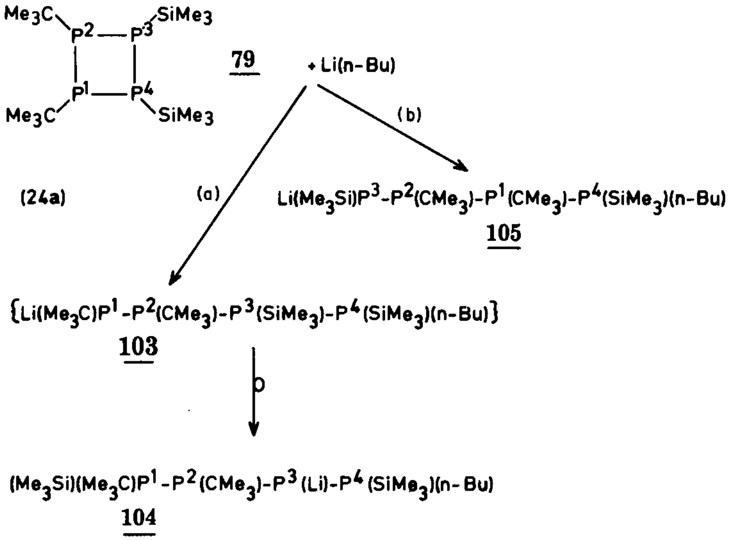
101 (**102**)

high solubility of the *n*-tetraphosphanes and the extreme tendency of their solutions to become supersaturated render their isolation as solid crystals quite difficult. Attempts to sublime such substances led to their thermal decomposition. Therefore, for their characterization by ^{31}P- and ^{1}H-NMR as well as for mass spectrometric investigations, the product mixtures—with the exception of compound **100**—as shown in Eq. (18) were used. In these mixtures the respective *n*-tetraphosphanes were present in proportions of 75–95%.

The multiple-step reaction of $P_4(SiMe_3)_3CMe_3$ with Li(*n*-Bu) and Me_3SiCl shown in Scheme 19 and in Eq. (18b) generate the *n*-tetraphosphane **100** with a 95% yield. During the final work-up, **100** is obtained initially as a colorless, highly viscous oil, which can occasionally become light yellow because of slight oxidation. By crystallization in a little *n*-pentane, colorless, rod-shaped crystals are obtained, which melt at 83 ± 3°C and gradually decompose. Compared with the cyclic tetraphosphane $P_4(SiMe_3)_3CMe_3$, the P—Si and P—P bonds in the *n*-tetraphosphane **100** differ distinctly in their behavior with Li(*n*-Bu). Whereas in $P_4(SiMe_3)_3CMe_3$ Li(*n*-Bu) (THF, −45°C) cleaves only a P—P bond and thus alters the phosphorus molecular skeleton, under comparable reaction conditions Li(*n*-Bu) cleaves an Si—P bond in compound **100**. As a result, *n*-$BuSiMe_3$ is eliminated and **96** is formed. This formation would seem, for steric and statistical reasons, unfavorable, but in terms of the fast isomerization of the primary *n*-tetraphosphide **94** into the secondary product **96** [Scheme 19, step (b)], this can be completely understood.

C. REACTIONS OF *cis*-$P_4(SiMe_3)_2(CMe_3)_2$(**79**) WITH *n*-BUTYLLITHIUM

The cyclotetraphosphane **79** is distinguished from its trans isomer (**82**) fundamentally by its reaction with Li(*n*-Bu). From **71** at 0°C/THF $LiP_4(CMe_3)_2SiMe_3$ (**70**) is formed by the cleavage of a P—Si bond; on the other hand, during the corresponding reaction of **79** between −30 and −25°C in THF, only P—P cleavage with resulting formation of open-chain *n*-tetraphosphides is observed. The behavior of **79** corresponds therefore to that of the more highly silylated homologs $P_4(SiMe_3)_4$ (**85**) and $P_4(SiMe_3)_3CMe_3$ (*44*). From the reaction of **79** with Li(*n*-Bu), various *n*-tetraphosphides can be expected as products of the ring opening. The nucleophilic attack of the butyl moiety occurs only on a silylated phosphorus atom of the four-membered ring [in Scheme 20 on P4], and causes the cleavage of the bond to one of the neighboring atoms P1 or P3. Both possibilities take place, although cleavage of the P4—P1 bond is preferred. According to Scheme 20, the *n*-tetraphosphides **104** and **105** are formed in a relative proportion of 10:3. The phosphide **103**, which could be thought of as a precursor of **104**, is not demonstrable, even though its formation from **79** and Li(*n*-Bu) as well as its rapid isomerization into **104**, according to the results given in paragraphs Sections VII,B,1 and VII,B,2, are absolutely plausible. A corresponding isomerization by means of a 1,3-displacement of lithium



SCHEME 20

cannot take place in the primary *n*-tetraphosphide **105** obtained as indicated in Scheme 20, because the corresponding phosphorus atom is blocked by the nonfunctional CMe_3 group.

Solutions of the *n*-tetraphosphides **105** and **104** in THF are intensely orange-red. Their decomposition takes place at −25°C within a few hours, and at room temperature within seconds, as shown by the color of the solution turning yellow. The compounds present after a reaction time of 15 days at 20°C [molar ratio **79**:Li(*n*-Bu) = 1:1] are $LiP_5(CMe_3)_4$ (**76**), $LiP_3(CMe_3)_2$ (**77**), $P_4(CMe_3)_4$ (**110**), $LiP(SiMe_3)_2$, *n*-$BuP(SiMe_3)_2$ (**111**), and $(Me_3C)P(SiMe_3)_2$. These results do not yet permit the formulation of detailed statements about the course of the reaction which yields the above compounds. Nevertheless they are certainly controlled decomposition reactions of the *n*-tetraphosphides formed from *cis*-$P_4(SiMe_3)_2(CMe_3)_2$ (**79**) and Li(*n*-Bu). And there exist certain analogies with the reactive behavior of $LiP[P(SiMe_3)CMe_3]_2$, which also yields **76** and **77**.

a. Preparation and Properties of the n-Tetraphosphanes from cis-$P_4(SiMe_3)_2(CMe_3)_2$. The thermolabile *n*-tetraphosphides **105** and **104** described in Section VII,B,3 were reacted with MeCl or Me_3SiCl immediately after their formation from **79** and Li(*n*-Bu) (*44*). The phosphides present in the mixture react with MeCl, as shown in Eqs. (19) and (20) between −30 and −35°C within a few minutes to yield the stable *n*-tetraphosphanes **108** and **109**.

$$\mathbf{107} + \mathrm{MeCl} \longrightarrow \underset{\mathbf{(108)}}{\mathrm{Me_3C(Me_3Si)P{-}P(CMe_3){-}P(Me){-}P(SiMe_3)(\mathit{n}\text{-}Bu)}} + \mathrm{LiCl} \quad (19)$$

$$\mathbf{105} + \mathrm{MeCl} \longrightarrow \underset{\mathbf{(109)}}{\mathrm{Me(Me_3Si)P{-}P(CMe_3){-}P(CMe_3){-}P(SiMe_3)(\mathit{n}\text{-}Bu)}} + \mathrm{LiCl} \quad (20)$$

These compounds could not be isolated in pure form. They appear during the final work-up of the reaction solution as viscous liquids which are colorless to light yellow and which mix well under all relative concentrations with the usual solvents and show no tendency whatsoever to crystallize. From the integration of the $^{31}P\{^1H\}$-NMR spectra of these mixtures, a ratio of 10:3 was established for the isomeric compounds **108** and **109**. This agrees with the ratio in the phosphides initially present (*44*). Although all the *n*-tetraphosphides so far described can be transformed into the corresponding silyl derivatives by reaction with Me_3SiCl, in the silylation of the phosphide **104** the following peculiarity is encountered.

$$\mathbf{104} \xrightarrow[-\mathrm{LiCl}]{+\mathrm{Me_3SiCl}} \underset{\mathbf{(110)}}{\{\mathrm{Me_3C(Me_3Si)P{-}P(CMe_3){-}P(SiMe_3){-}P(SiMe_3)}(n\text{-}\mathrm{Bu})\}} \qquad (21a)$$

$$\downarrow$$

$$\underset{\mathbf{(111)}}{\mathrm{P_3(CMe_3)_2SiMe_3}} + \underset{\mathbf{(113)}}{n\text{-}\mathrm{BuP(SiMe_3)_2}} \qquad (21b)$$

$$\mathbf{105} \xrightarrow[-\mathrm{LiCl}]{+\mathrm{Me_3SiCl}} \underset{\mathbf{(112)}}{\mathrm{(Me_3Si)_2P{-}P(CMe_3){-}P(CMe_3){-}P(SiMe_3)}(n\text{-}\mathrm{Bu})} \qquad (21c)$$

After warming the reaction mixture to 20°C the cyclotriphosphane **111** and **113** are formed, instead of the expected *n*-tetraphosphane **110**. Formation of **111** probably results from 1,3-elimination of *n*-$\mathrm{BuP(SiMe_3)_2}$ (**113**) from compound **110**. This preliminary step to the cyclization reaction, shown in Eq. (21b), could not be demonstrated, but nevertheless its formation according to Eq. (21a) and Eq. (19) is plausible. As is also shown by mass spectroscopic investigations, the *n*-tetraphosphanes exhibit a considerable tendency toward the formation of cyclotriphosphanes by means of 1,3-elimination of simpler phosphanes $\mathrm{RP(SiMe)_2}$ (*44*). The isomeric *n*-tetraphosphane **112** on the other hand, is stable in the same reaction solution.

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