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Silylphosphanes: Developments in Phosphorus Chemistry

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Contents

I. Introduction

Whereas molecular compounds containing bonds between elements of group 13 or 14 and group 15 as C−N, C−P, Si−N, and B−N have been known for a

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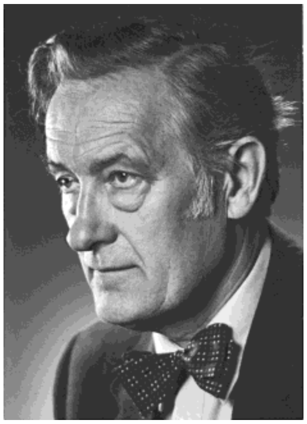


Gerhard Fritz was born in 1919 in Mittelhofen/Westerwald, Germany. He studied chemistry at the Universities of Halle-Wittenberg, Marburg, and Frankfurt/Main (interruptions due to World War II), where he obtained his Dr. rer. nat. in 1946 in the group of Prof. Dr. H. Hartmann (Physical Chemistry). He finished his habilitation in 1953 at the University of Marburg. In 1959 he became professor in Münster, in 1962 full professor in Giessen, and in 1965 full professor in Karlsruhe (TH), where he has been professor emeritus since 1980. His research interests are focused on the carbosilane chemistry, the chemistry of silylated phosphorus compounds, and phosphinophosphinidenes as ligands in transition metal complexes. Since 1972 he has been a member of the Academy of Science "Leopoldina" in Halle/Saale and of the Heidelberg Academy of Science since 1978. He has obtained many awards, e.g. the Kipping Award from the American Chemical Society in 1966, the Lavoisier Medal from the Société Francaise de Chimie in 1967, the Alfred-Stock-Memorial Award in 1967, and the Dr. rer. nat. h. c. of the University of Giessen in 1978.

Petra Scheer was born in 1960 in Riesa, Germany. She studied chemistry at the Martin-Luther University in Halle-Wittenberg beginning in 1980 and graduated in 1985 with the Diplom degree and 1988 as Ph.D. in the research group of Prof. Dr. A. Tzschach. From 1989 to 1993 she was research scientist in the Department of Medicine of the University Halle-Wittenberg. During this time she spent a year as a postdoctoral fellow in the group of Prof. D. Daleke in the Biochemistry Department at the University Bloomington, Indiana (USA). In 1995 she joined the group of Prof. Dr. D. Fenske at the University Karlsruhe, where she is currently working with Prof. Dr. Dr. h. c. G. Fritz.

long time, the chemistry of molecular compounds with Si−P bonds (silylphosphanes) was developed only in the second half of this century. The first representative of this class of substances was H_3Si-PH_2,[1] prepared by thermal decomposition of SiH_4 in the presence of PH_3 in order to examine the chemical behavior of the functional H−Si, H−P, and Si−P bonds. The salt elimination between polar Si- and P-compounds turned out to be useful for the formation of silylphosphanes even with various functional groups. The reaction of $LiPEt_2$ with Me_3SiCl yielded $Me_3Si-PEt_2$ for the first time, and reactions of $LiPMe_2$ with Me_2SiCl_2 or $SiCl_4$ opened the way to functional derivatives such as $Me_2ClSi-PMe_2$, $Cl_3Si-PMe_2$, and $(Me_2P)_2SiCl_2$.[2] Reactions of $LiPEt_2$ with $H_2(Ph)SiX$ (X = Cl, I) led to Si-functional silylphosphanes such as $H_2(Ph)Si-PEt_2$.[3] The synthesis of higher silylated phosphanes such as $EtP(SiMe_3)_2$ and $P(SiMe_3)_3$ and the cleavage of the Si−P bond by means of BuLi opened the way to $LiP(SiMe_3)_2{\cdot}THF$. The reaction of $LiP(SiMe_3)_2$ with various halides made it possible to transfer the $P(SiMe_3)_2$ group to many metals and nonmetals. The widespread use of $LiP(SiMe_3)_2{\cdot}THF$ in syntheses is due to the relatively convenient accessibility of $P(SiMe_3)_3$ by reacting P_4 with Na/K alloy and Me_3SiCl.[4] Nowadays, $LiP(SiMe_3)_2$ is the basic reagent for the formation of functional di-, tri-, and tetraphosphanes as well as of cyclic phosphanes with functional groups on selected P atoms.

Several reports dealing with certain areas in the chemistry of silylphosphanes are available.[5−9] The present review describes the basic processes in this field in a comprehensive way and includes such developments in phosphorus chemistry which rely on the use of silylphosphanes.

Phosphinophosphinidene phosphoranes, and especially the knowledge about their structures and formation reactions, open the access to a new class of metal complexes and open up new perspectives based on silylphosphanes. An analogous way leads into the chemistry of metal cluster compounds, which are interesting particularly with regard to developments of nano structures.[10] Important contributions to the scope of group 13/15 semiconductors and to formations of compounds with Si−P and P−C multiple bonds as well result from the chemistry of silylphosphanes.

The actual range of the chemistry of silylphosphanes can be traced back to reactions as selective Si−P bond formation and cleavage and to the stabilization of reactive P- or SiP-intermediates in consecutive reactions. The literature is covered including 1999.

II. Reactions with Cleavage of the Si−P Bond

Due to the different electronegativities of silicon and phosphorus, silylphosphanes react with suitable polar compounds in a clearly predictable manner under Si−P bond cleavage. Since these reactions are very typical for the chemistry of silylphosphanes and also offer a good understanding for such reactions, we have selected some characteristic examples for this introductory chapter. Detailed syntheses related to this reaction type will be discussed later. However, since cleavages of this Si−P bond occur in so many different reactions, they will appear throughout this paper again and again.

H_3Si-PH_2 (**1**) reacts with gaseous HBr as shown in (1).

$$\underset{\mathbf{1}}{H_3Si-PH_2} + HBr \rightarrow H_3SiBr + PH_3 \qquad (1)$$

The alkaline hydrolysis occurs as shown in (2).

$$\underset{\mathbf{1}}{H_3Si{-}PH_2} + 4H_2O \rightarrow Si(OH)_4 + 3H_2 + PH_3 \quad (2)$$

In the acidic aqueous hydrolysis H_2, PH_3, and SiH_4 were obtained as demonstrated in (3) and (4).[11]

$$\underset{\mathbf{1}}{H_3Si{-}PH_2} + H_2O \rightarrow H_3SiOH + PH_3 \quad (3)$$

$$H_3SiOH \rightarrow H_2 + SiH_4 + \text{Si-oxyhydrides} \quad (4)$$

This is in agreement with investigations related to the formation of $(H_3Si)_2O$.[12] In an analogous manner cleavages with alcohol in the presence of NaOEt are shown in (5) and (6).

$$\underset{\mathbf{1}}{H_3Si{-}PH_2} + EtOH \rightarrow H_3SiOEt + PH_3 \quad (5)$$

$$H_3SiOEt + 3EtOH \rightarrow Si(OEt)_4 + 3H_2O \quad (6)$$

Cleavage of the Si−P bond with HCl-saturated absolute ethyl alcohol at −80 °C occurs according to (5). Decomposition follows with increasing temperature (7).

$$H_3SiOEt \rightarrow H_2 + \text{trace SiH} + \text{SiH-containing polysilicic acid ester} \quad (7)$$

In liquid ammonia, **1** reacts under ammonolysis of the Si−P bond forming PH_3, SiH_4, and high-molecular SiN compounds of the type $[SiH_2(NH)]_x$.[13] Additionally, low-molecular compounds such as $(H_3Si)_2NH$ are formed which easily yield SiH_4 and $[SiH_2(NH)]_x$.[11] Non-metal halides, too, will cleave the Si−P bond, as is known from numerous examples.[14]

$$\underset{\mathbf{2}}{Me_3Si{-}PEt_2} + 2EtJ \rightarrow Me_3SiJ + (Et_4P)J \quad (8)$$

With $AlCl_3$ or AlH_2Cl, **2** forms an adduct, which yields cyclic Al−P compounds under elimination of Me_3SiCl or Me_3SiH after cleavage of the Si−P bond, as shown in (9) and (10).[15]

$$\underset{\mathbf{2a}}{Me_3Si{-}PEt_2{\cdot}AlCl_3} \rightarrow Me_3SiCl + {}^1/_3(Cl_2Al{-}PEt_2)_3 \quad (9)$$

$$\underset{\mathbf{2b}}{Me_3Si{-}PEt_2{\cdot}AlH_2Cl} \rightarrow Me_3SiH + {}^1/_3(HClAl{-}PEt_2)_3 \quad (10)$$

In an analogous manner cyclic B−P compounds were obtained when starting with boron halides, as demonstrated in (11)[16] and (12).[17]

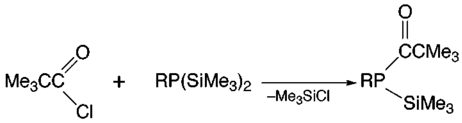
$$2Me_3Si{-}PEt_2{\cdot}BX_3 \rightarrow 2Me_3SiX + {}^1/_3(X_2B{-}PEt_2)_2 \quad (11)$$
$$X = Cl, \mathbf{2c};\ Br, \mathbf{2d}$$

$$\underset{\mathbf{1a}}{H_3Si{-}PH_2{\cdot}BCl_3} \rightarrow H_3SiCl + (1/n)(Cl_2B{-}PH_2)_n \quad (12)$$

Cleavage of silylphosphanes by means of acid chlorides provides a method for preparing the related acylphosphides by transfer of the phosphido group (13).[18]

$$\underset{\mathbf{3}}{Me_3Si{-}PPh_2} + RC(O)Cl \rightarrow RC(O)PPh_2 + Me_3SiCl \quad (13)$$

The versatility of the Si−P bond cleavage as an entrance to a sequence of stabilization reactions was demonstrated by Becker.[19] Their synthesis of the P=C double bond starts with a Si−P cleavage in $RP(SiMe_3)_2$ by means of pivalic chloride (14), followed by rearrangement and formation of the P=C double bond by migration of the silyl group (15).[19]



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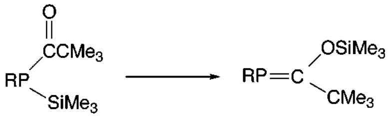


(15)

This reaction had an important influence on the development of the phosphaalkene chemistry.[20] Similarly, $P(SiMe_3)_3$ (**4**) yields $Me_3Si{-}P{=}C(OSiMe_3)t\text{Bu}$, which forms $t\text{BuC}{\equiv}P$, eliminating $(Me_3Si)_2O$ when catalyzed by sodium hydroxide.[21]

MeLi cleaves the Si−P bond according to (16).[22]

$$\underset{\mathbf{2}}{Me_3Si{-}PEt_2} + MeLi \rightarrow Si(Me_3)_4 + LiPEt_2 \quad (16)$$

III. Syntheses of Silylphosphanes

Because Si−R as well as P−R groups (R = alkyl, aryl) are fairly inert, the combination of halogenosilanes with alkali metal phosphanides each containing just one functional group proceed nearly without side reactions. If, however, more than one such substituent is present in the halogenosilane, secondary reactions under dismutation or transmetalation occur very easily. In contrast to alkali metal phosphanides, no transmetalations were observed in reactions with aluminates such as $NaAl(PHMe)_4$ or $LiAl(PMe_2)_4$.

A. Concepts and Problems in the Syntheses with Alkali Metal Phosphanides

Using this principle, a large amount of variously substituted compounds were synthesized with the Si−P unit having just one functional bond. As the first compound of this type, $Me_3Si{-}P(C_6H_5)_2$ (**3**) was prepared from Me_3SiCl and $NaP(C_6H_5)_2$.[23] Complications occur as soon as the starting compounds have more than one functional group.

So the reaction between H_3SiBr and KPH_2 does not lead to $H_3Si{-}PH_2$ (**1**), but transmetalation reactions of mono- and disilylated intermediates are responsible for the formation of $P(SiH_3)_3$ (**5**).[24] The preparation of pure, crystalline $LiPEt_2$ by Issleib and Tzschach[25] turned out to be a valuable basis for the systematic synthesis of Si-functional silylphosphanes containing the PEt_2 group, which are summarized with their NMR data in Tables 1 and 2.[26]

Whereas $Me_3Si{-}PEt_2$ (**2**) does not react with $LiPEt_2$, SiH-containing silylphosphanes with one PEt_2 group yield higher phosphanylated products according to (17) and (18).

$$\underset{\mathbf{6}}{H_3Si{-}PEt_2} + LiPEt_2 \rightarrow \underset{\mathbf{9}}{H_2Si(PEt_2)_2} + LiH \qquad (17)$$

$$\underset{\mathbf{7}}{H_2MeSi{-}PEt_2} + 2LiPEt_2 \rightarrow \underset{\mathbf{11}}{MeSi(PEt_2)_3} + 2LiH \qquad (18)$$

However there is a second reaction path which is preferred if the SiH-containing silylphosphane contains more than one PEt_2 group. $HSi(PEt_2)_3$ (**12**), e.g., reacts with $LiPEt_2$ by Li/H exchange (19).

$$\underset{\mathbf{12}}{HSi(PEt_2)_3} + LiPEt_2 \rightarrow \underset{\mathbf{13}}{LiSi(PEt_2)_3} + HPEt_2 \qquad (19)$$

With Me_3SiCl, **13** forms the disilane $Me_3Si{-}Si(PEt_2)_3$ (**14**), and with H_3SiBr, $H_3Si{-}Si(PEt_2)_3$ (**15**).[22]

B. SiHCl-Containing Silylphosphanes

Silylphosphanes with SiHCl groups in the molecule like **17**, available from H_3SiCl and $LiPEt_2$, and **19** are not stable and rearrange as shown in (20) and (21).

$$2\underset{\mathbf{17}}{HClSi(PEt_2)_2} \rightarrow \underset{\mathbf{9}}{H_2Si(PEt_2)_2} + \underset{\mathbf{18}}{Cl_2Si(PEt_2)_2} \qquad (20)$$

$$3\underset{\mathbf{19}}{H_2ClSi{-}PEt_2} \rightarrow 2\underset{\mathbf{6}}{H_3Si{-}PEt_2} + \underset{\mathbf{20}}{Cl_3Si{-}PEt_2} \qquad (21)$$

These reactions are not reversible because chlorosilylphosphanes such as **18** or **20**, e.g., react as cleaving element halides (22, 23)

$$\underset{\mathbf{18}}{Cl_2Si(PEt_2)_2} + \underset{\mathbf{9}}{H_2Si(PEt_2)_2} \rightarrow \underset{\mathbf{21}}{ClSi(PEt_2)_3} + \underset{\mathbf{19}}{H_2ClSi{-}PEt_2} \qquad (22)$$

$$\underset{\mathbf{20}}{Cl_3Si{-}PEt_2} + \underset{\mathbf{6}}{H_3Si{-}PEt_2} \rightarrow \underset{\mathbf{18}}{Cl_2Si(PEt_2)_2} + H_3SiCl \qquad (23)$$

quite similar to chlorosilanes (24).[27]

$$HSiCl_3 + \underset{\mathbf{6}}{H_3Si{-}PEt_2} \rightarrow \underset{\mathbf{22}}{HCl_2Si{-}PEt_2} + H_3SiCl \qquad (24)$$

H_3SiCl further disproportionates as dedicated in (25).[28]

$$4H_3SiCl \rightarrow 3SiH_4 + SiCl_4 \qquad (25)$$

Table 1. NMR Data of the Silylphosphanes $H_{3-x}Me_xSi{-}PR_2$ (R = Et, H, Me), $H_{3-x}Me_xSi{-}PHMe$ and $(H_{3-x}Me_xSi)_2PMe$ ($x = 0{-}3$)

R_3		$\delta(^1HSi)$ (ppm)	$\delta(^1HCSi)$ (ppm)	$\delta(^1HP)$ (ppm)	$\delta(^1HCP)$ (ppm)	$\delta(^{31}P)$ (ppm)	$^1J_{SiH}$ (Hz)	$^1J_{PH}$ (Hz)	$^2J_{PCH}$ (Hz)	$^2J_{PSiH}$ (Hz)	$^3J_{PSiCH}$ (Hz)	$^3J_{HSiPH}$ (Hz)	$^4J_{HSiPCH}$ (Hz)
$R_3Si{-}PEt_2$													
H_3	**6**	3.62	–				197 ± 0.5			16.6 ± 0.1	–		
H_2Me	**7**	3.88	0.25				190 ± 0.5			16.7 ± 0.1	4.2 ± 0.2		
HMe_2	**8**	4.08	0.21				185 ± 0.5			16.9 ± 0.2	4.0 ± 0.1		
Me_3	**2**	–	0.14				–			–	3.9 ± 0.1		
$R_3Si{-}PH_2$													
H_3	**1**	3.8 ± 0.02	–	1.35 ± 0.02		274 ± 1	208 ± 1	183.5 ± 1		16.7 ± 0.1		5.35 ± 0.1	
H_2Me	**31**	4.1 ± 0.02	0.37 ± 0.02	1.29 ± 0.02		256 ± 1	198 ± 1	181.5 ± 1		18.65 ± 0.1	3.5 ± 0.1	4.65 ± 0.1	
HMe_2	**32**	4.37 ± 0.05	0.3 ± 0.05	1.23 ± 0.05		244 ± 1	195 ± 1	181 ± 1		21.5 ± 0.1	3.9 ± 0.1	4.15 ± 0.1	
$HMeSi(PH_2)_2$	**33**	4.64 ± 0.02	0.55 ± 0.02	1.52 ± 0.02		233.5 ± 1	204 ± 1	180 ± 3		20.8 ± 0.1	3.8 ± 0.2	4.2 ± 0.2	
$R_3Si{-}PHMe$													
H_3	**34**	3.76 ± 0.02	–	2.17 ± 0.05	1.12 ± 0.02	202 ± 1	201 ± 1	186 ± 3	3.7 ± 0.2		–	4.9 ± 0.1	0.35 ± 0.1
H_2Me	**35**	4.03 ± 0.02	0.3 ± 0.02	2.07 ± 0.05	1.06 ± 0.02	190 ± 1	195.5 ± 1	187 ± 3	3.0 ± 0.2		3.9 ± 0.1	4.3 ± 0.1	–
HMe_2	**36**	4.23 ± 0.02	0.22 ± 0.01	1.94 ± 0.05	1.00 ± 0.02	181 ± 1	191 ± 1	188 ± 3	3.0 ± 0.2		3.9 ± 0.1	3.7 ± 0.1	–
Me_3	**37**	–	0.2 ± 0.02	1.83 ± 0.05	0.97 ± 0.02	175 ± 1	–	188 ± 3	2.8 ± 0.2		4.05 ± 0.1	–	–
$R_3Si{-}PMe_2$													
H_3	**42**	3.65 ± 0.02	–		1.13 ± 0.02	143.2 ± 1	196.5 ± 1		3.45 ± 0.1	16.4 ± 0.1	–		0.35 ± 0.1
H_2Me	**43**	3.85 ± 0.02	0.23 ± 0.02		1.08 ± 0.02	138 ± 1	190.5 ± 1		3.15 ± 0.1	17.3 ± 0.1	4.4 ± 0.1		0.25 ± 0.1
HMe_2	**44**	4.02 ± 0.02	0.18 ± 0.02		1.03 ± 0.02	135.1 ± 1	186.5 ± 1		2.8 ± 0.1	17.0 ± 0.1	4.3 ± 0.1		–
Me_3	**45**	–	0.11 ± 0.02		0.98 ± 0.02	132 ± 1	–		2.6 ± 0.1	–	3.95 ± 0.1		–
$(R_3Si)_2PMe$													
H_3	**38**	3.83 ± 0.02	–		1.17 ± 0.02	253 ± 1	204 ± 1		3.15 ± 0.1	17.4 ± 0.1	–		
H_2Me	**39**	4.04 ± 0.02	0.32 ± 0.02		1.07 ± 0.02	232 ± 1	196.5 ± 1		2.5 ± 0.1	17.0 ± 0.1	4.8 ± 0.1		
HMe_2	**40**	4.22 ± 0.02	0.21 ± 0.02		0.97 ± 0.02	213 ± 1	190 ± 1		2.1 ± 0.1	15.5 ± 0.1	4.7 ± 0.1		
Me_3	**41**	–	0.19 ± 0.02		1.02 ± 0.02	197 ± 1	–		1.65 ± 0.1	–	4.4 ± 0.1		

Table 2. NMR Data of the Silylphosphanes $R_2Si(PEt_2)_2$ (R_2 = H_2, HMe, Me_2), $RSi(PEt_2)_3$ (R = H, Me), and $R_3Si{-}Si(PEt_2)_3$ (R_3 = H_3, HMe_2, Me_3)

compd		$\delta(^1HSi)$ (ppm)	$\delta(^1HCSi)$ (ppm)	$^1J_{SiH}$ (Hz)	$^2J_{PSiH}$ (Hz)	$^3J_{PSiCH}$ (Hz)	$^3J_{HCSiH}$ (Hz)	$^3J_{HCSi-Si}$ (Hz)	$^3J_{HSi-SiP}$ (Hz)
$R_2Si(PEt_2)_2$									
$R_2 = H_2$	**9**	3.95	–	189 ± 0.5	14.9 ± 0.1	3.35 ± 0.1	4.3 ± 0.1		
R_2 = HMe	**10**	4.08	0.31	185 ± 0.5	15.2 ± 0.1	3.5 ± 0.1	–		
$RSi(PEt_2)_3$									
R = H	**12**	4.21	–	182 ± 1.0	14.6 ± 0.1	–			
R = Me	**11**	–	0.36	–	–	3.55 ± 0.1			
$R_3SiSi(PEt_2)_3$									
$R_3 = H_3$	**15**	3.32	–				–	–	2.75
$R_3 = HMe_2$	**16**	4.15	0.31				4.6	2.6 ± 0.2	2.1
$R_3 = Me_3$	**14**	–	0.26				–	2.3	–

Some silylphosphanes containing SiH, but no SiMe groups disproportionate at 20 °C within a few months:

$$\underset{\mathbf{6}}{2H_3Si{-}PEt_2} \rightarrow SiH_4 + \underset{\mathbf{9}}{H_2Si(PEt_2)_2} \quad (26)$$

$$\underset{\mathbf{12}}{2HSi(PEt_2)_3} \rightarrow \underset{\mathbf{9}}{H_2Si(PEt_2)_2} + \underset{\mathbf{23}}{Si(PEt_2)_4} \quad (27)$$

$H_2Si(PEt_2)_2$ (**9**) is stable under the same conditions.

SiMe-containing silylphosphanes such as $H_2MeSi{-}PEt_2$ (**7**) and $MeSi(PEt_2)_3$ (**11**) are stable, distillable compounds. To prepare pure SiH-containing derivatives, the HSiCl group can be transferred into the H_2Si group with LiH.[27]

C. Silylphosphanes with PH Groups

Via a radical mechanism the thermal decomposition of SiH_4 above 450 °C in the presence of PH_3 yielded $H_3Si{-}PH_2$ (**1**)[1] as well as higher boiling derivatives.[29] Despite the fact that, as a result of these reactions, the properties of these compounds could be determined, this is not at all an ideal synthetic way to silylphosphanes with PH groups.

A Si−P bond formation from H_3SiX (X = halogen) and MPH_2 (M = Na, Li, K) is not generally realizable, because $NaPH_2$ and KPH_2 are not sufficiently soluble in ether. So these phosphanides are not suitable for the transfer of PH_2 groups.[30]

With PH_3, Li forms $LiPH_2{\cdot}4NH_3$ in liquid ammonia, but since NH_3 has to be removed prior to any further synthetic steps, the adduct then yields Li_2PH.[31] $LiPH_2$, obtained from PH_3 and LiPh in Et_2O,[32] additionally contains Li_2PH and Li_3P.[25] That is why from this starting reaction a controlled synthesis of pure silylphosphanes is not achievable.

To realize the synthesis of functional silylphosphanes, easily soluble and purely accessible phosphanides are required. Several phosphanylated aluminates proved able to fulfill these demands. As shown in (28), the reaction of $AlCl_3$ with $LiPEt_2$ gives $LiAl(PEt_2)_4$, which is easily soluble in THF.[33]

$$AlCl_3 + 4LiPEt_2 \rightarrow LiAl(PEt_2)_4 + 3LiCl \quad (28)$$

The AlH-containing derivatives $LiAlH_n(PEt_2)]_{4-n}$ were prepared according to (29)[34] and (30).[35]

$$H_2AlCl + 2LiPEt_2 \rightarrow LiAlH_2(PEt_2)_2 + LiCl \quad (29)$$

$$AlH_3 + LiPEt_2 \rightarrow LiAlH_3(PEt_2) \quad (30)$$

As the first PH_2-substituted compound of this type, $LiAl(PH_2)_4$ is accessible according to (31).[36]

$$LiAlH_4 + 4PH_3 \rightarrow LiAl(PH_2)_4 + 4H_2 \quad (31)$$

However, on a preparative scale, the use of this reaction is rather limited due to long reaction times and the formation of nonseparable mixtures of $LiAlH_4$ and $LiAlH_n(PH_2)_{4-n}$. A more convenient method is the synthesis of $NaAl(PH_2)_4$ based on the formation of $NaPH_2$ in liquid ammonia.[37]

$$Na + PH_3 \rightarrow NaPH_2 + {}^1\!/_2H_2 \quad (32)$$

After removal of NH_3, $NaPH_2$ has to be dissolved in diglyme and reacted with $AlCl_3$ (33).

$$4NaPH_2 + AlCl_3 \rightarrow NaAl(PH_2)_4 + 3NaCl \quad (33)$$

In the same way, $NaAl(PHMe)_4$ is obtainable from $MePH_2$.

The formation of LiPHMe, necessary for the preparation of $LiAl(PHMe)_4$, is given in (34).

$$MePH_2 + LiC_4H_9 \rightarrow LiPHMe + C_4H_{10} \quad (34)$$

The subsequent reaction with $AlCl_3$ proceeds similar to (33).[38]

$LiAl(PHMe)_4$ cannot be obtained from $LiAlH_4$ and $MePH_2$; the only product obtained even after long reaction times is $LiAlH(PHMe)_3$.[39]

The above-mentioned aluminates are soluble in diglyme and triglyme. Due to microcrystalline, precipitated NaCl, milky suspensions are formed, which can directly be used for further reactions.

The specified aluminates allow the phosphanylation of silicon halides without any problems. Treatment of $LiAl(PH_2)_4$ with H_3SiBr, H_2SiBr_2, or $HSiBr_3$ leads to the silylphosphanes **1**, $H_2Si(PH_2)_2$ (**24**), or $HSi(PH_2)_3$ (**25**), respectively, which are sensitive to oxidation.[40] With $SiCl_4$ in tetraethylene glycol dimethyl ether at −30 °C, the colorless, crystalline $Si(PH_2)_4$ (**26**) (mp, −25 °C) was obtained in addition to $HSi(PH_2)_3$ (**25**) and PH_3. Compound **26** was characterized by ^1H and ^{31}P NMR spectra as well as by a X-ray crystal structure analysis performed at 243 K.[41] The silylphosphanes $RSi(PH_2)_3$ with R = Me (**27**), Et (**28**), *i*Pr (**29**), and Ph (**30**), resulted from the reaction of $LiAl(PH_2)_4$ with $RSiCl_3$.[42]

As shown in (35), the silylphosphanes **1**, **31**, and **32** could be obtained in yields of more than 65%.

$$\mathrm{NaAl(PH_2)_4} + \underset{\substack{x=0\\ x=1\\ x=2}}{4\mathrm{H}_{3-x}\mathrm{Me}_x\mathrm{SiBr}} \rightarrow \underset{\substack{\mathbf{1}\\ \mathbf{31}\\ \mathbf{32}}}{4\mathrm{H}_{3-x}\mathrm{Me}_x\mathrm{Si{-}PH_2}} + \mathrm{NaAlBr_4} \tag{35}$$

Other than in the reaction of KPH_2 with H_3SiBr leading unexpectedly to $P(SiH_3)_3$ (**5**),[24] no transmetalations were observed. $HMeSi(PH_2)_2$ (**33**) can be prepared in the same way as shown in (35) by reaction with $HMeSiCl_2$. Starting from $NaAl(PHMe)_4$ the silylphosphanes **34**−**37** were successfully prepared according to (36) and (37).

$$\mathrm{NaAl(PHMe)_4} + \underset{\substack{x=0\\ x=1\\ x=2}}{4\mathrm{H}_{3-x}\mathrm{Me}_x\mathrm{SiBr}} \rightarrow \underset{\substack{\mathbf{34}\\ \mathbf{35}\\ \mathbf{36}}}{4\mathrm{H}_{3-x}\mathrm{Me}_x\mathrm{Si{-}PHMe}} + \mathrm{NaAlBr_4} \tag{36}$$

$$\mathrm{NaAl(PHMe)_4} + 4\mathrm{Me_3SiCl} \rightarrow \underset{\mathbf{37}}{4\mathrm{Me_3Si{-}PHMe}} + \mathrm{NaAlBr_4} \tag{37}$$

The PHMe-containing silylphosphanes were obtained only in yields between 55 and 66%, because additionally $MePH_2$ and a disilylphosphane of the type $(R_3Si)_2PMe$ were formed by a dismutation process as shown in (38).

$$\underset{\substack{\mathbf{34}\quad x=0\\ \mathbf{35}\quad x=1\\ \mathbf{36}\quad x=2\\ \mathbf{37}\quad x=3}}{2\mathrm{H}_{3-x}\mathrm{Me}_x\mathrm{Si{-}PHMe}} \rightarrow \underset{\substack{\mathbf{38}\\ \mathbf{39}\\ \mathbf{40}\\ \mathbf{41}}}{(\mathrm{H}_{3-x}\mathrm{Me}_x\mathrm{Si})_2\mathrm{PMe}} + \mathrm{MePH_2} \tag{38}$$

Such dismutations proceed preferably in the reaction mixture; the isolated pure compounds were found to be clearly more stable.[38] NMR data of the mentioned silylphosphanes with PH_2 and PHMe groups are listed in Table 1.

D. Silylphosphanes $H_{3-x}Me_xSi{-}PMe_2$

Whereas soluble compounds such as $LiPEt_2$ and $LiAl(PEt_2)_4$ are well-suited to introduce the PEt_2 group into silanes, the reaction of the poorly soluble $LiPMe_2$ with chlorosilanes in ether is considerably more complicated, as is evident from side products and small yields.[43]

Due to secondary reactions the metalation of $HPMe_2$ cannot be performed similar to the formation of $NaPH_2$ from PH_3 and sodium in liquid NH_3.[44] However, the lithiation can be realized with BuLi in diglyme at −50 °C, as shown in (39).

$$\mathrm{HPMe_2} + \mathrm{BuLi} \rightarrow \mathrm{LiPMe_2} + \mathrm{C_4H_{10}} \tag{39}$$

$$4\mathrm{LiPMe_2} + \mathrm{AlCl_3} \rightarrow \mathrm{LiAl(PMe_2)_4} + 3\mathrm{LiCl} \tag{40}$$

According to (40) the target lithium alanate is obtainable at low temperature as a clear, yellow-brown solution in diglyme without ether cleavage. Using aliquot parts of this solution, **42** was prepared in a yield of 65% according to (41), whereas **43**−**45** were obtained in yields between 70 and 75%.[45]

$$\mathrm{LiAl(PMe_2)_4} + \underset{\substack{x=0,\ \mathrm{X}=\mathrm{Br}\\ x=1,\ \mathrm{X}=\mathrm{Br}\\ x=2,\ \mathrm{X}=\mathrm{Br}\\ x=3,\ \mathrm{X}=\mathrm{Cl}}}{4\mathrm{H}_{3-x}\mathrm{Me}_x\mathrm{SiX}} \rightarrow \underset{\substack{\mathbf{42}\\ \mathbf{43}\\ \mathbf{44}\\ \mathbf{45}}}{4\mathrm{H}_{3-x}\mathrm{Me}_x\mathrm{Si{-}PMe_2}} + \mathrm{LiAlX_4} \tag{41}$$

The NMR data of these silylphosphanes are summarized in Table 1.

IV. Silylphosphanes $H_mMe_nX_{3-(n+m)}Si{-}PH_2$ (X = Cl, Br, F)

Reactions of halogenosilanes with silylphosphanes of the type $R_2Si(PH_2)_2$ under cleavage of one Si−P bond yield in a first step silylphosphanes which contain a halogeno substituent as an additional Si-functional group. In many cases, secondary reactions involving the various functional groups designate the final composition of the products.

$HMeClSi{-}PH_2$ (**46**) is formed in 40% yield without side products according to (42) during 48 h at 80 °C in a sealed Pyrex ampule.

$$\mathrm{HMeSiCl_2} + \underset{\mathbf{33}}{\mathrm{HMeSi(PH_2)_2}} \rightarrow \underset{\mathbf{46}}{2\mathrm{HMeClSi{-}PH_2}} \tag{42}$$

Any modifications of the reaction conditions such as temperature, reaction time, and molar ratio of the reactants were found to enhance the side reactions. So a reaction at 80 °C with $MeSiHCl_2$ in an excess of 20% after 120 h yields a mixture of $H_2MeSiCl$, $HMeSiCl_2$, $MeSiCl_3$, **31**, **46**, **33**, $MeCl_2Si{-}PH_2$ (**47**), $MeClSi(PH_2)_2$ (**48**), and $MeSi(PH_2)_3$ (**27**) (Table 3). At 100 °C (10 h) the same compounds are formed.

A comparable synthesis with $SiBr_4$ at room temperature proceeds more clearly. A product mixture of $H_2MeSiBr{:}Br_3Si{-}PH_2 = 4{:}1$ is obtained after 10 days, as shown in (43).

$$\underset{\mathbf{31}}{\mathrm{H_2MeSi{-}PH_2}} + \mathrm{SiBr_4} \rightarrow \mathrm{H_2MeSiBr} + \underset{\mathbf{49}}{\mathrm{Br_3Si{-}PH_2}} \tag{43}$$

Table 3. NMR Data of the Methylsilylphosphanes $H_mMe_nX_{3-(n+m)}Si-PH_2$ (X = Cl, Br; $m = 0, 1$; $n = 1$)

compd		$\delta(^1HSi)$ (ppm)	$\delta(^1HCSi)$ (ppm)	$\delta(^1HP)$ (ppm)	$\delta(^{31}P)$ (ppm)	$^1J_{SiH}$ (Hz)	$^1J_{PH}$ (Hz)	$^2J_{PSiH}$ (Hz)	$^3J_{PSiCH}$ (Hz)	$^3J_{HSiPH}$ (Hz)	$^4J_{HCSiPH}$ (Hz)
$HMeClSi-PH_2$	**46**	5.36 ± 0.02	0.74 ± 0.02	1.72 ± 0.02	229.5 ± 1	237 ± 1	186 ± 1	22.4 ± 1	3.25 ± 0.1	3.3 ± 0.1	0.25 ± 0.1
$MeCl_2Si-PH_2$	**47**		1.02 ± 0.02	2.06 ± 0.02	213.5 ± 2		186.5 ± 1		1.7 ± 0.2		0.4 ± 0.1
$HMeBrSi-PH_2$	**50**	5.18 ± 0.02	0.90 ± 0.02	1.95 ± 0.02	226 ± 1		186.5 ± 1	21.7 ± 0.2	3.0 ± 0.1	3.4 ± 0.1	
$MeClSi(PH_2)_2$	**48**		0.93 ± 0.02	1.98 ± 0.02	2.9 ± 2		186.5 ± 2		3.2 ± 0.1		0.3 ± 0.1

Table 4. NMR Data of the Halogen-Containing Silylphosphanes with the PH_2 Group

compd		$\delta(^1HP)$ (ppm)	$\delta(^{31}P)$ (ppm)	$\delta(^{19}F)$ (ppm)	$^1J_{PH}$ (Hz)	$^1J_{SiP}$ (Hz)	$^2J_{SiPH}$ (Hz)	$^2J_{PSiF}$ (Hz)	$^3J_{HPSiF}$ (Hz)	$^1J_{SiF}$ (Hz)
F_3Si-PH_2	**54**	1.56 ± 0.02	290 ± 1	117 ± 0.3	194.5 ± 1	15.0 ± 0.2	13.1 ± 0.1	23.6 ± 0.1	4.2 ± 0.1	331 ± 1
$F_2BrSi-PH_2$	**53**	2.04 ± 0.02	243 ± 1	98.5 ± 0.3	190 ± 1			11.7 ± 0.2	5.3 ± 0.1	370 ± 2
FBr_2Si-PH_2	**52**	2.63 ± 0.02	207 ± 1	88.3 ± 0.3	189 ± 1	55 ± 1		0.75 ± 0.1	5.75 ± 0.1	407 ± 1
Br_3Si-PH_2	**49**	3.14 ± 0.02	174 ± 1		188 ± 1	65 ± 1	12.0 ± 0.1			
$Br_2Si(PH_2)_2$	**51**	2.85 ± 0.02	181 ± 1		189 ± 1					
$BrSi(PH_2)_3$	**57**	2.52 ± 0.02	192 ± 1		189 ± 1					
Cl_3Si-PH_2	**58**	2.38 ± 0.02	205 ± 1		186.5 ± 1	48.8 ± 0.3	12.3 ± 0.1			

Due to a subsequent decomposition of **49**, some PH_3 is observed. Using an excess of **31** increased the reaction speed but decreased the yield of **49**. $HMeSi(PH_2)_2$ (**33**) reacts faster with $SiBr_4$ than **31**. From a reaction with a molar ratio of 1:1 at 20 °C after 14 h a mixture of **33**, $HMeBrSi-PH_2$ (**50**), **49**, $HMeSiBr_2$, and PH_3 in a ratio of 2:1:0.5:0.25:0.2 was obtained. Within 8 days the silylphosphanes **33** and **50** disappeared completely from the reaction mixture, whereas the amount of PH_3 increased. Then, the volatile compounds $HMeSiBr_2$, **49**, and $Br_2Si(PH_2)_2$ (**51**) were isolated in a molar ratio of 4:2:1. The reaction starts as shown in (44) followed by a second step according to (45).

$$\underset{\mathbf{33}}{HMeSi(PH_2)_2} + SiBr_4 \rightarrow \underset{\mathbf{50}}{HMeBrSi-PH_2} + \underset{\mathbf{49}}{Br_3Si-PH_2} \quad (44)$$

$$\underset{\mathbf{50}}{HMeBrSi-PH_2} + SiBr_4 \rightarrow HMeSiBr_2 + \underset{\mathbf{49}}{Br_3Si-PH_2} \quad (45)$$

SiF_4 does not react with PH_2-containing silylphosphanes, but with the compounds F_nSiBr_{4-n} the Si−P bond cleavage is initiated by the SiBr group. The reaction between $FSiBr_3$ and **33** at 20 °C proceeds as shown in (46).

$$\underset{\mathbf{33}}{HMeSi(PH_2)_2} + FSiBr_3 \rightarrow \underset{\mathbf{50}}{HMeBrSi-PH_2} + \underset{\mathbf{52}}{FBr_2Si-PH_2} \quad (46)$$

After 17 h the reaction mixture contains starting compounds and products in the same ratio. Compound **52** decomposes at 20 °C, resulting in SiH_4, PH_3, and **51**, whereas $F_2BrSi-PH_2$ (**53**) and F_3Si-PH_2 (**54**) appear as intermediates (Table 4). F_3SiBr forms **54** and **50** with **33**. However, only 65% of the starting compounds have reacted at 20 °C after 24 h. Meanwhile, F_3Si-PH_2 (**54**) decomposes already yielding SiF_4, PH_3, and F_3SiBr.[46] Since the preparative isolation of **54** from the reaction mixture is rather difficult, the reaction according to (47) offers a more convenient route with 60% yield to this compound. Secondary products are SiF_4 and traces of PH_3.

$$4F_3SiBr + MAl(PH_2)_4 \xrightarrow[\text{M = Li, Na}]{} 4\underset{\mathbf{54}}{F_3Si-PH_2} + MAlBr_4 \quad (47)$$

$F_2Si(PH_2)_2$ (**55**) and $FSi(PH_2)_3$ (**56**) cannot be obtained by an analogous reaction of F_2SiBr_2 or $FSiBr_3$. Instead SiF_4, PH_3, and **54** are formed in agreement with the dismutation reaction of the bis- and tris-substituted intermediates as observed in the previously discussed reactions with F_2SiBr_2 and $FSiBr_3$. At 20 °C, **54** is a low-viscousity, colorless liquid (molecular weight: found, 117.6; calculated, 118 from vapor density).

As compared to H_3Si-PH_2 (**1**), the SiF_3 group in **54** causes a lower basicity of the P atom. Whereas $JP(CF_3)_2$ cleaves **1** at −25 °C within 2 days completely, the reaction with **54** at 20 °C takes 5 days. Investigations of the adduct formation of **54** or **1** with BCl_3, $AlCl_3$, or $AlBr_3$ confirm these observations. The lower stability of the adduct $F_3Si-PH_2{\cdot}BCl_3$ (**54a**) allows for a reversible dissociation in its components, whereas in case of $H_3Si-PH_2{\cdot}BCl_3$ (**1a**) the required higher temperature leads to Si−P bond cleavage. Closely above the melting point of **54** an unstable adduct with BBr_3 is formed, but immediately a continuous gas formation was observed (48).

$$\underset{\mathbf{54}}{F_3Si-PH_2} + BBr_3 \xrightarrow[-78\ ^\circ C]{} \underset{\mathbf{54b}}{F_3Si-PH_2{\cdot}BBr_3} \xrightarrow[-78\ ^\circ C]{} F_3SiBr + (1/n)(Br_2B-PH_2)_n \quad (48)$$

F_3SiBr was obtained in a yield of 80% related to **54**.[47]

V. Metalation of the PH_2 Group in Silylphosphanes

The lithiation of the PH_2 group in silylphosphanes is of special interest with respect to the synthesis of higher molecular derivatives. A PHLi group can be achieved using either nBuLi or LiPHMe, a PLi_2 group using Li_2PEt or nBuLi in the appropriate stoichio-

metric ratio. In certain syntheses, the use of LiAl(HP−SiH$_{3-x}$Me$_x$)$_4$ instead of the related LiHP-derivatives causes considerably less undesired side reactions.

Silylphosphanes containing only SiH and PR$_2$ groups such as HSi(PEt$_2$)$_3$ (**12**) with LiPEt$_2$ form LiSi(PEt$_2$)$_3$ (**13**) and HPEt$_2$.[22] If, however, a PH$_2$ group is present, lithiated products result, as shown in (49).

$$\begin{array}{ll}\mathrm{H_{3-x}Me_xSi{-}PH_2} + 2\mathrm{LiPEt_2} \xrightarrow[(2)\ +20\ ^\circ\mathrm{C}]{(1)\ -80\ ^\circ\mathrm{C}} & \\ \quad x = 0,\ \mathbf{1} & \\ \quad x = 1,\ \mathbf{31} & \\ \quad x = 2,\ \mathbf{32} & \\ \quad x = 3,\ \mathbf{59} & \\ & \begin{array}{c}\mathrm{H_{3-x}Me_xSi{-}PLi_2} + 2\mathrm{HPEt_2}\\ \mathbf{60}\\ \mathbf{61}\\ \mathbf{62}\\ \mathbf{63}\end{array}\end{array} \tag{49}$$

For final identification the dimetalated products were treated with MeCl to form the P-methylated silylphosphanes **42**−**45** according to (50).

$$\begin{array}{ll}\mathrm{H_{3-x}Me_xSi{-}PLi_2} + 2\mathrm{MeCl} \rightarrow & \\ \quad x = 0,\ \mathbf{60} & \\ \quad x = 1,\ \mathbf{61} & \\ \quad x = 2,\ \mathbf{62} & \\ \quad x = 3,\ \mathbf{63} & \\ & \begin{array}{c}\mathrm{H_{3-x}Me_xSi{-}PMe_2} + 2\mathrm{LiCl}\\ \mathbf{42}\\ \mathbf{43}\\ \mathbf{44}\\ \mathbf{45}\end{array}\end{array} \tag{50}$$

The corresponding reactions with 1 mol of LiPEt$_2$ proceed in a more complicated way as was demonstrated by investigations of **31** in diglyme between +20 and −78 °C.[48a] It is not possible to prepare silylphosphanes with the PHLi group by this path.

A. Formation and Reactions of H$_{3-x}$Me$_x$Si−PHLi

Norman published the preparation of **59** and Me$_2$Si(PH$_2$)$_2$[48b] (**64**) and the monolithiation of the PH$_2$ group with *n*BuLi in THF (molar ratio 1:1), giving rise to the silylphosphanides Me$_3$Si−PHLi (**68**) or Me$_2$Si(PH$_2$)PHLi (**69**), respectively, and to the bislithio product Me$_2$Si(PHLi)$_2$ (**70**) with additional *n*BuLi. Reactions of **68** with alkyl and alkenyl halides such as MeI, CH$_2$═CHCH$_2$Br and CH$_2$═CHCH$_2$CH$_2$Br lead to the methylated derivative H$_3$Si−PHMe (**37**) and to the alkenyl(silyl)phosphanes CH$_2$═CHCH$_2$P(H)SiMe$_3$ (**71**) and CH$_2$═CHCH$_2$CH$_2$P(H)SiMe$_3$ (**72**), respectively. The formation of **72** is also accompanied by significant amounts of CH$_2$═CHCH$_2$CH$_2$P(SiMe$_3$)$_2$ (**73**). The bisphosphanes Me$_2$Si(PH$_2$)PHMe (**74**) and Me$_2$Si(PHMe)$_2$ (**75**) were accessible by treating **69** and **70** with MeI. The reaction of BrCH$_2$CH$_2$CH$_2$Br with **70** proceeds cleanly to form the six-membered ring Me$_2$Si[(H)P(CH$_2$)$_3$P(H)] (**76**). All mentioned compounds were comprehensively characterized by ^{1}H, ^{13}C, and ^{31}P NMR, MS, and IR investigations.[48c]

Whereas LiPEt$_2$ was found to substitute all protons of the PH$_2$ group in related silylphosphanes, compounds of the type H$_{3-x}$Me$_x$Si−PHLi are accessible by using LiPHMe according to (51), which does not form dimetalated derivatives due to its low base strength. LiPHMe was formed from MePH$_2$ and BuLi in DME.

$$\begin{array}{ll}\mathrm{H_{3-x}Me_xSi{-}PH_2} + \mathrm{LiPHMe} \rightarrow & \\ \quad x = 0,\ \mathbf{1} & \\ \quad x = 1,\ \mathbf{31} & \\ \quad x = 2,\ \mathbf{32} & \\ \quad x = 3,\ \mathbf{59} & \\ & \begin{array}{c}\mathrm{H_{3-x}Me_xSi{-}PHLi} + \mathrm{MePH_2}\\ \mathbf{65}\\ \mathbf{66}\\ \mathbf{67}\\ \mathbf{68}\end{array}\end{array} \tag{51}$$

According to (51), MePH$_2$ is isolated in 93−100% yield with only 1−5% PH$_3$. Even in the case of higher LiPHMe amounts (ratio 1:2) no further PH metalation occurs. The equimolar solution of LiPHMe and **65**, resulting from the reaction of **1** with LiPHMe in a molar ratio of 1:2, decomposes within a few days under development of H$_2$ and formation of a white precipitate. Solutions with concentrations higher than 0.1 mol/L of the monometalated silylphosphanes in DME and diglyme dismutate according to (52), either at warming to room temperature or adding nonpolar solvents (benzene, pentane) as was shown by NMR investigations (Table 5).

$$\begin{array}{lcl}2\mathrm{H_{3-x}Me_xSi{-}PHLi} & \rightleftarrows & \mathrm{(H_{3-x}Me_xSi)_2PLi} + \mathrm{LiPH_2}\\ \quad x = 0,\ \mathbf{65} & & \quad \mathbf{77}\\ \quad x = 1,\ \mathbf{66} & & \quad \mathbf{78}\\ \quad x = 2,\ \mathbf{67} & & \quad \mathbf{79}\\ \quad x = 3,\ \mathbf{68} & & \quad \mathbf{80}\end{array} \tag{52}$$

After reaching the equilibrium of (52), the solutions are stable at 20 °C for several days. LiP(SiMe$_3$)$_2$ (**80**) reacts with LiPH$_2$ in diglyme or DME overnight, forming **68**. The required LiPH$_2$ is accessible by treating PH$_3$ in diglyme with LiPEt$_2$. From the solutions (according to (52)) first of all LiPH$_2$ has to be separated by evaporating the solvent and by adding benzene. Then the intended disilylphosphanides may be isolated as colorless solid etherates after crystallization from Et$_2$O at −40 °C. In benzene they react with CH$_3$Cl to form the well-known disilylmethylphosphanes, as shown in (53).

$$\begin{array}{ll}\underset{\mathbf{80a}}{\mathrm{LiP(SiMe_3)_2{\cdot}DME}} + \mathrm{CH_3Cl} \rightarrow & \\ & \underset{\mathbf{41}}{\mathrm{MeP(SiMe_3)_2}} + \mathrm{LiCl} + \mathrm{DME}\end{array} \tag{53}$$

With halogenosilanes the corresponding trisilylphosphanes were formed according to (54) and (55).

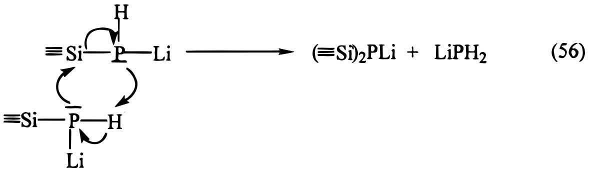
$$\begin{array}{ll}\underset{\mathbf{80a}}{\mathrm{LiP(SiMe_3)_2{\cdot}DME}} + \mathrm{Me_3SiCl} \rightarrow & \\ & \underset{\mathbf{4}}{\mathrm{P(SiMe_3)_3}} + \mathrm{LiCl} + \mathrm{DME}\end{array} \tag{54}$$

$$\begin{array}{ll}\underset{\mathbf{78a}}{\mathrm{LiP(SiMeH_2)_2{\cdot}2DME}} + \mathrm{H_2MeSiBr} \rightarrow & \\ & \underset{\mathbf{81}}{\mathrm{P(SiMeH_2)_3}} + \mathrm{LiBr} + 2\mathrm{DME}\end{array} \tag{55}$$

Table 5. NMR Data of the Silylphosphanes $R_3SiPHLi$, $HP(SiR_3)_2$, $LiP(SiR_3)_2$, $P(SiR_3)_3$, ($R_3 = H_{3-x}Me_x$)

R_3		$\delta(^1HSi)$ (ppm)	$\delta(^1HCSi)$ (ppm)	$\delta(^1HP)$ (ppm)	$\delta(^{31}P)$ (ppm)	$^1J_{SiH}$ (Hz)	$^1J_{PH}$ (Hz)	$^2J_{PSiH}$ (Hz)	$^3J_{PSiCH}$ (Hz)	$^3J_{HSiPH}$ (Hz)	$^1J_{SiP}$ (Hz)
$R_3Si-PHLi$											
H_3	**65**	4.03 ± 0.02		−2.26 ± 0.02	349 ± 1		144 ± 1	16.5 ± 0.5		6.0 ± 0.1	
H_2Me	**66**		0.14 ± 0.02	−2.2 ± 0.02	314 ± 1		146.2 ± 1	19.0 ± 0.5	2.4 ± 0.1	5.5 ± 0.1	
HMe_2	**67**		0.09 ± 0.02	−1.85 ± 0.05	295 ± 1		150.0 ± 1	18.0 ± 0.1	2.85 ± 0.1	3.8 ± 0.1	
Me_3	**68**	–	0.06 ± 0.02	−1.89 ± 0.03	287 ± 1		152 ± 1	–	2.9 ± 0.1	–	
$HP(SiR_3)_2$											
H_3	**85**	3.85 ± 0.02	–	0.63 ± 0.02		212 ± 1	183 ± 1	16.9 ± 0.1		5.0 ± 0.1	34.8 ± 0.3
H_2Me	**82**	4.16 ± 0.02	0.36 ± 0.02	0.65 ± 0.02		202 ± 1	183 ± 1	17.1 ± 0.1	4.4 ± 0.1	4.4 ± 0.1	30.3 ± 0.3
HMe_2	**86**	4.32 ± 0.02	0.29 ± 0.02	0.50 ± 0.02		198.5 ± 1	183 ± 1	14.9 ± 0.1	4.55 ± 0.1	3.35 ± 0.1	27.0 ± 0.3
Me_3	**87**	–	0.26 ± 0.02	0.51 ± 0.02		–	185.5 ± 1	–	4.4 ± 0.1	–	25.0 ± 0.3
$LiP(SiR_3)_2$											
H_3	**77**	4.05 ± 0.02	–		–			–	–		
H_2Me	**78**	4.29 ± 0.02	0.15 ± 0.02		355 ± 1			16.8 ± 0.1	2.95 ± 0.1		
HMe_2	**79**	4.16 ± 0.02	0.13 ± 0.02		317 ± 1			14.8 ± 0.1	3.3 ± 0.1		
Me_3	**80**	–	0.10 ± 0.02		301 ± 1				3.4 ± 0.1		
$P(SiR_3)_3$											
H_3	**5**	3.93 ± 0.02	–		378 ± 1	211 ± 1		17.0 ± 0.1	–		42.2 ± 0.3
H_2Me	**81**	4.16 ± 0.02	0.37 ± 0.02		328 ± 1	202		15.5 ± 0.1	5.2 ± 0.1		37.0 ± 0.3
HMe_2	**88**	4.47 ± 0.02	0.33 ± 0.02		284 ± 1	194 ± 1		14.5 ± 0.1	4.9 ± 0.1		32.0 ± 0.3
Me_3	**4**	–	0.27 ± 0.02		251 ± 1	–		–	4.5 ± 0.1		27.5 ± 0.3

The dismutation in (52) follows a four-center mechanism as demonstrated in (56).



Only about 65% of the expected $MePH_2$ was obtained in addition to 35% PH_3, if the reaction of (51) was performed in triglyme at −40 °C (57).

$$R_3Si{-}PH_2 + LiPH_2 \rightarrow R_3SiPHLi + PH_3 \quad (57)$$

The amounts of PH_3 and $MePH_2$ add up to 100%. Both side reactions do not influence the reactions in diglyme or DME. LiPHMe is stable in diglyme at 20 °C; therefore, ether cleavage reactions can be excluded.

With CH_3Cl the monometalated PH-containing silylphosphanes do not exclusively produce the intended PH-containing silylmethylphosphanes. Thus, $H_2MeSi-PHLi$ (**66**) with CH_3Cl yields a product mixture containing $MePH_2$, $H_2MeSi-PHMe$ (**35**), $H_2MeSi-PMe_2$ (**43**), $(H_2MeSi)_2PMe$ (**39**), and $(H_2MeSi)_2O$. $MePH_2$ and **39** result from the reaction of CH_3Cl with the dismutation products of **66** (52). Transmetalation is responsible for the presence of **43**. Also ether cleavage occurs as the formation of $(H_2MeSi)_2O$ shows. The reaction of **66** with $H_2MeSiBr$ yields $HP(SiMeH_2)_2$ (**82**) and $P(SiMeH_2)_3$ (**81**) in a ratio of 1:6. Besides of the intended disilylphosphanes, also trisilylphosphanes were formed.[48a]

B. Formation of $LiAl(HPSiH_3)_4$ and $LiAl(HPSiMeH_2)_4$ As Well As Their Reactions with MeCl, $H_2MeSiBr$, and H_3SiBr

The undesired formation of trisilylphosphanes when treating $H_{3-x}Me_xSi-PHLi$ with halogenosilanes corresponds to the reaction of KPH_2 with H_3SiBr, yielding $P(SiH_3)_3$ (**5**).[24] This difficulty can be avoided by using the milder reacting $LiAl(PHMe)_4$.[38]

The synthesis of this compound from LiPHMe and $AlCl_3$ can be transferred to that of monometalated silylphosphanes at −40 °C in diglyme according to (58).

$$\begin{aligned} &4H_{3-x}Me_xSi{-}PHLi + AlCl_3 \rightarrow \\ &\quad x = 0,\ \mathbf{65} \\ &\quad x = 1,\ \mathbf{66} \\ &\qquad\qquad \underset{\mathbf{83}\ \mathbf{84}}{LiAl(HP{-}SiH_{3-x}Me_x)_4} + 3LiCl \quad (58) \end{aligned}$$

Corresponding syntheses in DME fail because of the low solubility of $AlCl_3$. In triglyme other secondary reactions prevent the formation of single products.

The reaction of $LiAl(HP-SiMeH_2)_4$ (**84**) with MeCl proceeds as shown in (59).

$$\begin{aligned} &\underset{\mathbf{84}}{LiAl(HP{-}SiMeH_2)_4} + 4MeCl \rightarrow \\ &\qquad 4\underset{\mathbf{35}}{H_2MeSi{-}PHMe} + AlCl_3 + LiCl \quad (59) \end{aligned}$$

Compound **82** (obtained according to (60)) dismutates to form $H_2MeSi-PH_2$ (**31**) and **81**. Since this is favored by $AlBr_3$, only a fast isolation from the reaction mixture gives access to the disilylphosphane.

$$\begin{aligned} &\underset{\mathbf{84}}{LiAl(HP{-}SiMeH_2)_4} + 4H_2MeSiBr \rightarrow \\ &\qquad 4\underset{\mathbf{82}}{HP(SiMeH_2)_2} + AlBr_3 + LiBr \quad (60) \end{aligned}$$

In the same way the reaction with H_3SiBr proceeds (61), followed by a partial dismutation of the formed disilylphosphane (**85**) (62). The compounds **85** and **5** were isolated by fractional condensation.

$$\begin{aligned} &\underset{\mathbf{83}}{LiAl(HP{-}SiH_3)_4} + 4H_3SiBr \rightarrow \\ &\qquad 4\underset{\mathbf{85}}{HP(SiH_3)_2} + AlBr_3 + LiBr \quad (61) \end{aligned}$$

$$2\underset{\mathbf{85}}{HP(SiH_3)_2} \rightarrow \underset{\mathbf{1}}{H_3Si{-}PH_2} + \underset{\mathbf{5}}{P(SiH_3)_3} \quad (62)$$

As resulted from NMR investigations, the three products **85**, **1**, and **5** were obtained in the same ratio. Metalation of these silylphosphanes with BuLi are more complex due to additional cleavages of the Si−P bond.[22,48a]

Various parallel reactions may occur when treating monometalated silylphosphanes ≡SiPHLi with MeCl or halogenosilanes. Besides the desired silylphosphanes, some compounds are always present in the product mixture formed by dismutation as well as by ether cleavage.

However, in most cases uniform substances are formed in the transformation of the silylphosphanes ≡SiPHLi with $AlCl_3$ to the silylated tetraphosphinoaluminates. The cleavage of the Al−P bond in these aluminates with MeCl yields the intended compounds with PHMe groups. With halogenosilanes the expected disilylphosphanes are formed initially but have to be separated immediately from the reaction mixture to prevent the subsequent dismutation to mono- and trisilylphosphanes. Such complications did not occur in PH-free metalated silylphosphanes.

VI. Bis(trialkylsilyl)phosphanides of Alkali and Bivalent Metals

Alkali metal bis(trimethylsily)phosphanides represent an easily prepared class of compounds with a high synthetical potential with respect to functional silylphosphanes. This synthetic utility resulted in considerable interest in the structural chemistry. Silylated phosphido complexes of alkaline earth metals as well as of group 12 metals gained interest with regard to formation of coordination compounds. The structures of the phosphanides are determined by the participation of solvent molecules and by the steric demands of the Si substituents.

A. Formation

The crystalline $LiP(SiMe_3)_2 \cdot DME$ (**80a**) can be synthesized via lithiation of $Me_3Si{-}PH_2$ (**59**) to $Me_3Si{-}PHLi$ (**68**) and subsequent rearrangement of **68**,[48a] but it is considerably more convenient to start from **4**, which can be prepared either according to (63)[4,49] or by reacting phosphorus with sodium and Me_3SiCl.[50]

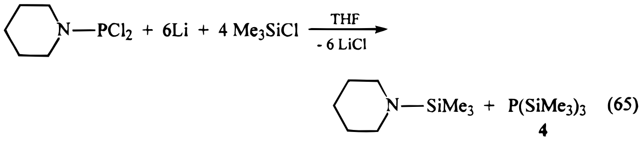
$$3K/Na + P_4 \rightarrow (K_3P/Na_3P) \xrightarrow[\substack{-3KCl \\ -3NaCl}]{+3Me_3SiCl} \underset{\mathbf{4}}{P(SiMe_3)_3} \quad (63)$$

After metalation with BuLi the monolithiated silylphosphanide **80a** can be isolated as a colorless, crystalline etherate between −40 and −30 °C in 65−75% yield (64).

$$\underset{\mathbf{4}}{P(SiMe_3)_3} + BuLi \rightarrow \underset{\mathbf{80a}}{LiP(SiMe_3)_2 \cdot DME} + Me_3SiBu \quad (64)$$

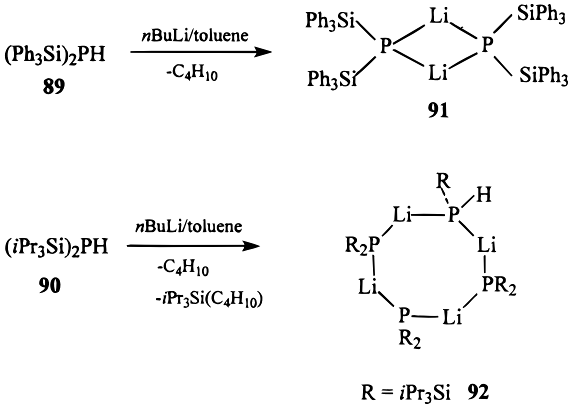
After long reaction times (26 h, −30 °C) 10−20% of the applied BuLi may be consumed by ether cleavage. Correspondingly, $LiP(SiMe_3)_2 \cdot 2THF$ (**80b**) can be prepared at −30 °C and recrystallized from toluene. In pentane at 20 °C, **4** does not react with BuLi, but with a stoichiometric amount of DME the reaction starts forming **80a** in a yield of 13%, whereas 54% of **4** was recovered. The ether-free **80** is accessible by treating $HP(SiMe_3)_2$ (**87**) with BuLi in pentane.[51]

Still another path to $P(SiMe_3)_3$ **4** starts from piperidyldichlorophosphane according to (65).[52]



(65)

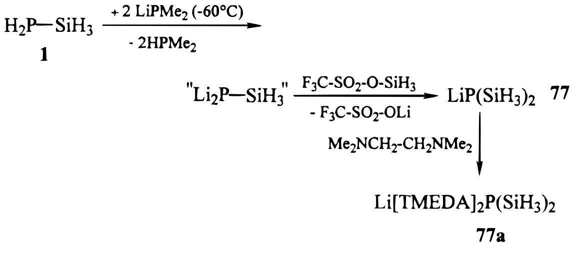
The lithiation of the bulky disilylphosphanes $HP(SiR_3)_2$ (R = Ph (**89**), *i*Pr (**90**)) with *n*BuLi at 0 °C in toluene proceeds in different directions. In the case of **90** a Si−P bond cleavage was observed as a competition reaction, additionally to *n*BuSi*i*Pr₃, the phosphanide being formed. The phosphanides were isolated as two different aggregates **91** and **92** in the shape of colorless crystals (66).



(66)

The required silylphosphanes $HP(SiR_3)_2$ (R = Ph (**89**), *i*Pr (**90**)) are accessible by simple salt elimination from $LiPH_2 \cdot DME$ and either the chlorosilane Ph_3SiCl or silyltrifluoromethanesulfonate $iPr_3SiOSO_2CF_3$.[53]

$[TMEDA]_2LiP(SiH_3)_2$ (**77a**) can be prepared by lithiation of **1** in DME at −60 °C and subsequent monosilylation with silyl trifluoromethanesulfonate, followed by complexation according to (67).



(67)

As found by an X-ray structure determination, the colorless cuboids of **77a** contain isolated ions $[(TMEDA)_2Li]^+$ and $[P(SiH_3)_2]^-$.[54]

Silylphosphanides of other alkali metals such as $MP(SiMe_3)_2$ (M = Na, K) are accessible in a preparative scale by treating **87**, which can be obtained by hydrolysis of **4**, with the metal hydrides NaH or KH, respectively (68).

$$\underset{\mathbf{87}}{HP(SiMe_3)_2} + MH \rightarrow \underset{\substack{\mathbf{93},\ M = Na\\ \mathbf{94},\ M = K}}{MP(SiMe_3)_2} + H_2 \tag{68}$$

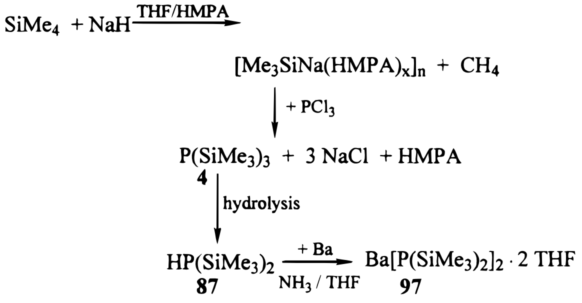
Even the usage of metal hydrides can be avoided, if **87** is allowed to react directly with the alkali metal in strongly solvating solvents in the presence of a condensed aromatic compound, such as naphthalene. Following this reaction route all alkali metal bis(trimethylsilyl)phosphanides $MP(SiMe_3)_2$ (M = Li–Cs) could be synthesized.[55a] The transmetalation of $LiP(SiMe_3)_2{\cdot}2THF$ (**80b**) with KO*t*Bu offers another synthetic route for producing **94**.[55b] Moreover, **4** reacts with the *tert*-butyl alcoholates of all alkali metals to form the corresponding bis(trimethylsilyl)phosphanides (69).

$$\underset{\mathbf{4}}{P(SiMe_3)_3} + MOtBu \rightarrow MP(SiMe_3)_2 + Me_3SiOtBu \tag{69}$$

$$M = Li,\ \mathbf{80};\ Na,\ \mathbf{93}^{55c}$$
$$M = K,\ \mathbf{94};\ Rb,\ \mathbf{95};\ Cs,\ \mathbf{96}$$

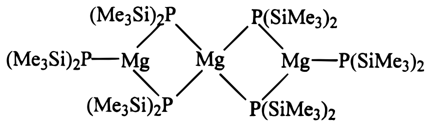
The synthetic versatility of this route is demonstrated by the wide choice of possible phosphane reagents. Analogous reactions of organosubstituted silylphosphanes $RP(SiMe_3)_2$ (with R = alkyl, aryl) result in (trimethylsilyl)organophosphanides $MP(R)(SiMe_3)$, while (trimethylsilyl)diorgano-substituted phosphanes $R_2P(SiMe_3)$ give rise to diorgano-substituted phosphanides MPR_2. Investigations in cleaving all P–Si bonds in **4** with an excess of potassium *tert*-butanolate to produce the trimetalated K_3P were not successful even after extended reflux in THF. Only the monometalated product **94** could be isolated in excellent yields. The compounds $MP(SiMe_3)_2$ (M = K, Rb, Cs) were characterized by X-ray crystallography. They display polymeric ladder-type structures such as $[Rb(THF)P(SiMe_3)_2]_\infty$ (Figure 4).[55d]

With regard to their reactivity and structure, major differences exist between bis(trialkylsilyl)phosphanides of alkaline metals and alkaline earth metals. With metallic barium, $HP(SiMe_3)_2$ (**87**) reacts rapidly to the barium silylphosphanide $Ba[P(SiMe_3)_2]_2{\cdot}2THF$ (**97**) in a mixed liquid ammonia–THF solvent system (70). For the preparation of **4**, an alternative high-yield synthetic route was developed, which involves the reaction of tetramethylsilane and sodium hydride in a solvent mixture of THF and HMPA (2:1) followed by the dropwise addition of PCl_3. Eventually, **4** was converted into **87** by controlled hydrolysis.[56]



(70)

$Mg[P(SiMe_3)_2]_2{\cdot}TMEDA$ (**98**) was synthesized by reacting magnesium dibutanide $MgBu_2$ with **87**. Recrystallization of **98** from THF–pentane solution yields $Mg[P(SiMe_3)_2]_2{\cdot}2THF$ (**98a**).[57a] A solution of magnesium bis[bis(trimethylsilyl)phosphanide] in toluene shows a dimer–trimer equilibrium at −40 °C with an increasing amount of the dimer with increasing temperature, as monitored by ^{31}P NMR. Colorless crystals of the trimeric



form (crystal structure analysis) precipitate at −30 °C from the solution.[57b] The addition of THF yields the already known $Mg[P(SiMe_3)_2]_2{\cdot}2THF$ (**98a**).[57c]

A solvent-free hexameric magnesium tri(*tert*-butyl)silylphosphanediid $[MgPSitBu_3]_6$ (**99**) was isolated as yellow cuboids from the metalation of $H_2P{-}SitBu_3$ (**100**) with $MgBu_2$.[57d] If the isopropyl-substituted silylphosphane $HP[Si(H)iPr_2]_2$ (**101**) in toluene is metalated with $MgBu_2$, the solvent-free, dimeric $[Mg\{P[Si(H)iPr_2]_2\}_2]_2$ (**102**) was available. The metathesis reaction of $(DME)LiPH_2$ and $ClSi(H)iPr_2$ offers an easy approach to $HP[Si(H)iPr_2]_2$ (**101**), which is obtained together with $P[Si(H)iPr_2]_3$ (**103**).[57b]

Alkaline earth metal bis(trialkylsilyl)amides have proved to be excellent starting substances for the preparation of the corresponded phosphanides. In such metal complexes, the $N(SiMe_3)_2$ ligand can be replaced by $P(SiMe_3)_2$ (71). Additionally, the adduct ligand (L) will be replaced by THF.

$$M[N(SiMe_3)_2]_2{\cdot}2L + 2\underset{\mathbf{87}}{HP(SiMe_3)_2} \xrightarrow[-2HN(SiMe_3)_2]{THF} M[P(SiMe_3)_2]_2{\cdot}xTHF \tag{71}$$

$$\begin{aligned} M &= Mg,\ \mathbf{98a},\ x = 2\\ M &= Ca,\ \mathbf{104},\ x = 3\\ M &= Sr,\ \mathbf{105},\ x = 3\\ M &= Ba,\ \mathbf{97a},\ x = 4 \end{aligned}$$

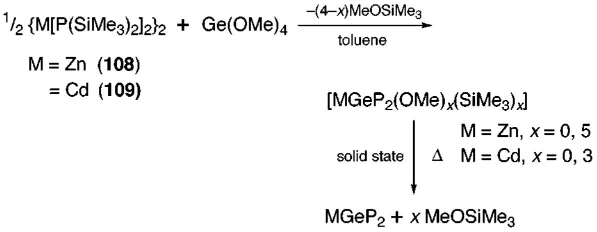
The THF content increases from $x = 2$ in the case of magnesium up to $x = 4$ in the case of barium. The molecule of $Ba[P(SiMe_3)_2]_2{\cdot}4THF$ (**97a**) was characterized by an X-ray structure determination.[57a]

In an analogous manner the triisopropylsilylphosphane $H_2P{-}SiiPr_3$ (**106**), available from $(DME)LiPH_2$ and $ClSiiPr_3$, can be metalated by the dimeric $\{Ca[N(SiMe_3)_2]_2\}_2$ [57d] and by the THF adduct $(THF)_2M[N(SiMe_3)_2]_2$ (M = Ca, Ba).[57f] Depending on the stoichiometry of the reactants, also mixed alkaline earth metal–amide–phosphanides were produced. When choosing an equimolar ratio of **106** and $Ca[N(SiMe_3)_2]_2$ in DME, the dimeric $\{(Me_3Si)_2NCa(DME)[\mu\text{-}P(H)SiiPr_3]\}_2$ (**106a**) is successfully formed. The complex $\{(Me_3Si)_2NCa[\mu\text{-}P(H)SiiPr_3]\}_3Ca(THF)_3$ (**106b**) was isolated by using the phosphanide **106** and $Ca[N(SiMe_3)_2]_2$ in THF in a molar ratio of 3 to 2. Its bicyclic structure was deduced from NMR experiments. If in this metalation tetrahydropyran (THP) serves as the solvent, the bicyclic complex $\{(Me_3Si)_2NCa[\mu\text{-}P(H)SiiPr_3]\}_3Ca(THP)_3$ (**106c**) was obtained and its structure characterized to have a trigonal-bipyramidal Ca_2P_3 core.[57f] Using the 2-fold molar ratio of **106** leads quantitatively to the phosphanide $Ca[P(H)Si\mathit{i}Pr_3]_2(THF)_4$ (**106d**), which in the presence of 1 equiv of bis[bis(trimethylsilyl)amino]stannylene forms a stable derivative, as demonstrated in (72).[57e] Barium bis[bis(trimethylsilyl)-

$$\underset{\mathbf{106d}}{2(THF)_4Ca[PHSi(\mathit{i}Pr)_3]_2} + Sn[N(SiMe_3)_2]_2 \rightarrow [Ca_2(THF)_5][\langle\{(\mathit{i}Pr)_3SiP\}_2Sn\{PHSi(\mathit{i}Pr)_3\}\rangle \cdot PHSi(\mathit{i}Pr)_3] + 2HN(SiMe_3)_2 + 3THF \quad (72)$$

amide] metalates 2 equiv of **106** in THF to give the bicyclic $(THF)_3Ba[\mu\text{-}P(H)Si\mathit{i}Pr_3]Ba(THF)_2P(H)Si\mathit{i}Pr_3$ (**107**), whereas the reaction of equimolar amounts of $(THF)_2Ba[N(SiMe_3)_2]_2$ and $H_2P{-}Si\mathit{t}Bu_3$ **100** in toluene quantitatively affords the heteroleptic dimeric $\{(THF)_2Ba[N(SiMe_3)_2][P(H)Si\mathit{t}Bu_3]\}_2$ (**107a**), featuring a Ba_2P_3 ring. Addition of a further equivalent silylphosphane **100** leads to the formation of $(THF)_n\text{-}Ba[P(H)Si\mathit{t}Bu_3]_2$ (**107b**).[57f]

The preparation of the silylmethyl-substituted phosphido complexes $M[P(SiMe_3)_2]_2$ of the metals Zn (**108**), Cd (**109**), Hg (**110**), Sn (**111**), Pb (**112**), and Mn (**113**) succeeds in a synthetic route, quite analogously to (71). All products are crystalline solids. X-ray crystallography reveals that **108**, **109**, **110**, and **112** are solid-state dimers having the structure $\{M[P(SiMe_3)_2(\mu\text{-}P(SiMe_3)_2]_2\}_2$. Compound **113** crystallizes as a THF adduct; however, the THF ligand can easily be removed in vacuo. The complexes exhibit varying degrees of thermal stability, decreasing in solution from **108** up to **112**. Both phosphido complexes $M[P(SiMe_3)_2]_2$ (M = Zn (**108**), Cd (**109**)) have been used as precursors for the preparation of semiconductors. Amorphous Cd_3P_2 results from the methanolysis of **109**. Heating the amorphous material to 600 °C leads to polycrystalline Cd_3P_2. The ternary phosphides $ZnGeP_2$ and $CdGeP_2$ could be obtained according to (73) after thermal treatment.[58a]



$$\tfrac{1}{2}\{M[P(SiMe_3)_2]_2\}_2 + Ge(OMe)_4 \xrightarrow[\text{toluene}]{-(4-x)MeOSiMe_3} [MGeP_2(OMe)_x(SiMe_3)_x] \qquad (73)$$

M = Zn (**108**)
= Cd (**109**)

$$[MGeP_2(OMe)_x(SiMe_3)_x] \xrightarrow[\Delta]{\text{solid state}} MGeP_2 + x\,MeOSiMe_3 \qquad M = Zn,\ x = 0,5;\ M = Cd,\ x = 0,3$$

The bulky disilylphosphido complexes $M[P(SiPh_3)_2]_2$ of the metals Zn, Cd, Hg, and Sn could be isolated after purification as crystalline solids (Zn, Cd, Hg) or powder (Sn) in 50−90% yields (74).

$$M[N(SiMe_3)_2]_2 + \underset{\mathbf{91}}{2LiP(SiPh_3)_2} \rightarrow M[P(SiPh_3)_2]_2 + 2LiN(SiMe_3)_2$$
$$(M = Zn\ (\mathbf{108a}),\ Cd\ (\mathbf{109a}),\ Hg\ (\mathbf{110a}),\ Sn\ (\mathbf{111a})) \qquad (74)$$

$Cd[P(SiPh_3)_2]_2$ (**109a**) forms unstable adducts with pyridine and PMe_3. The $M[P(SiPh_3)_2]_2$ compounds exhibit considerably higher thermal stabilities and insensitivity to air than the $\{M[P(SiMe_3)_2]_2\}_2$ analogue. Also the structures are different. Whereas the silylphenyl-substituted compounds adopt monomeric structures, $\{M[P(SiMe_3)_2]_2\}_2$ are dimeric and possess both bridging and terminal $P(SiMe_3)$ ligands (except M = Hg (**110**)[58a]).[58b]

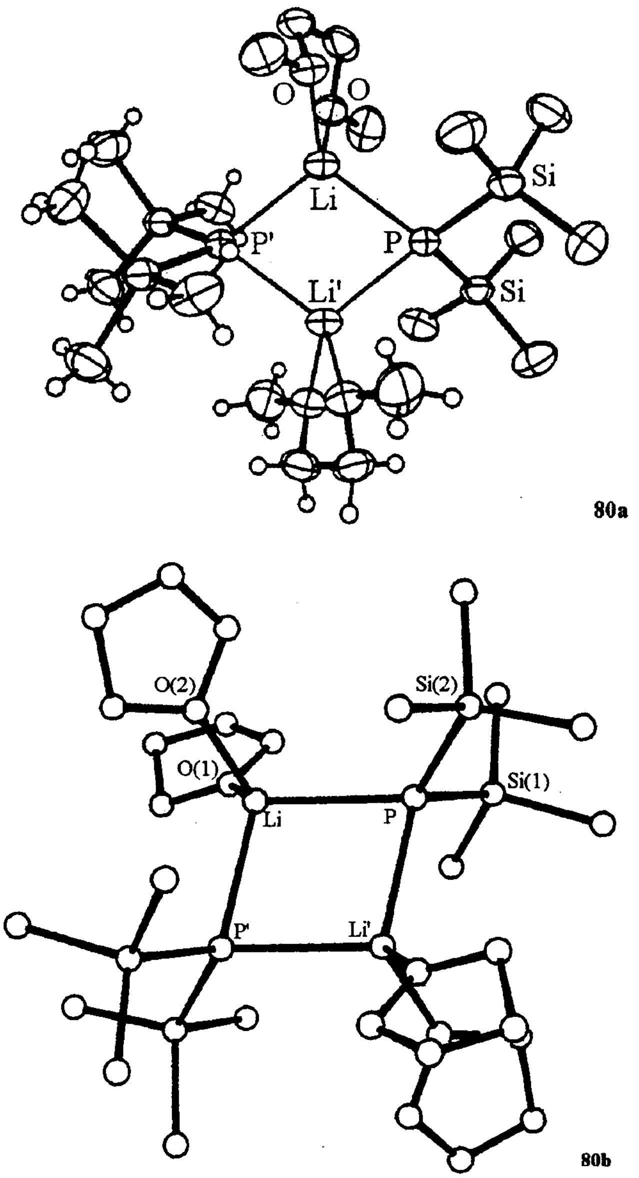


Figure 1. Molecular structure of **80a** and $[Li\{\mu\text{-}P(SiMe_3)_2\text{-}(THF)_2]_2$ (**80b**). Reprinted with permission from ref 59. Copyright 1989 Wiley-VCH Verlag GmbH. Reprinted with permission from ref 60. Copyright 1987 Elsevier Science Ltd.

B. Structures

In this part, especially the lithium phosphanides will be dealt with, whose structures are influenced by the formation of intermolecular donor−acceptor bonds between phosphorus and lithium. However, the degree of association is decisively determined by the space requirement of the substituents at the phosphorus atom and by the electronic saturation of the Li center by external donor ligands.[53] The different solvent molecules coordinated in solid $LiP(SiMe_3)_2$ **80** determine which crystal structures will be adopted by the compounds. Compounds **80a** [59] and **80b** [60] are dimeric in the solid state with a planar 2,4-dilithia-1,3-diphosphetane ring (Figure 1).

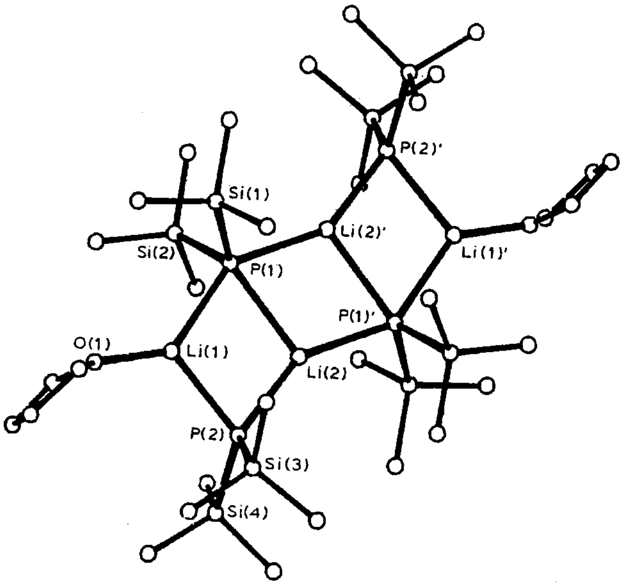


Figure 2. Molecular structure of $Li_4\{\mu_2\text{-}P(SiMe_3)_2\}_2\{\mu_3\text{-}P(SiMe_3)_2\}_2(THF)_2$ (**80c**). Reprinted with permission from ref 60. Copyright 1987 Elsevier Science Ltd.

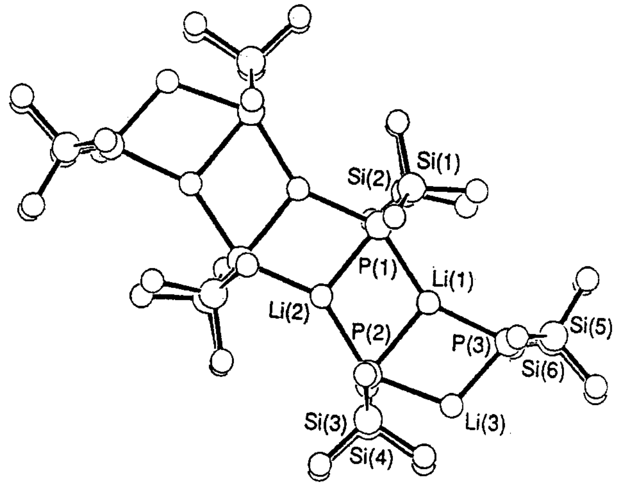


Figure 3. Molecular structure of the hexameric $LiP(SiMe_3)_2$ (**80**). Reprinted with permission from ref 63. Copyright 1992 Royal Society of Chemistry.

$[Li\{\mu\text{-}P(CH(SiMe_3)_2\}_2]_2$ [61] and $[LiPPh(SiMe_3)(TMEDA)]_2$ [62] have structures of the same type. Different just by its lower content of THF, $LiP(SiMe_3)_2\cdot 0.5THF$ (**80c**) would better be written as $Li_4\{\mu_2\text{-}P(SiMe_3)_2\}_2\{\mu_3\text{-}P(SiMe_3)_2\}_2(THF)_2$, which forms a ladder with four Li−P steps (Figure 2).[60]

The crystal structure of the solvent-free **80** [51] shows a hexameric arrangement with 4 five-coordinated and 2 four-coordinated P atoms as well as 4 three-coordinated and 2 two-coordinated Li atoms. The compound forms a ladder with six Li−P steps according to Figure 3.[63]

The bis(trimethylsilyl)phosphanides of the heavier alkali metals K, Rb, and Cs display ladder-type structures, too (Figure 4).[55d]

The crystalline $LiPH_2\cdot DME$, which is stable at room temperature and soluble in THF, is formed in the reaction of PH_3 with *n*BuLi in DME.[64] $LiPH_2\cdot DME$ with BuLi (molar ratio 1:1) forms Li_2PH.[65] In solid $LiPH_2\cdot DME$ the PH_2 groups and the Li·DME units are arranged in an alternating sequence. Due to the nearly linear Li−P−Li blocks (angle Li−P−Li = 177°) the polymeric screws oriented along [010] degenerate to chiral zigzag chains (angle P−Li−P = 118°), as shown in Figure 5.[59]

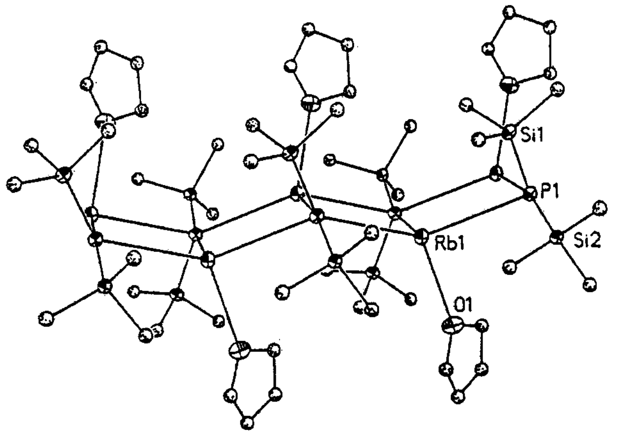


Figure 4. Molecular structure of $[Rb(THF)P(SiMe_3)_2]_n$. Reprinted with permission from ref 55d. Copyright 1998 American Chemical Society.

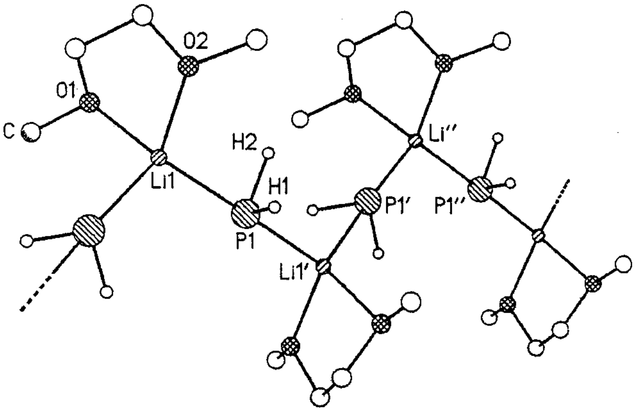
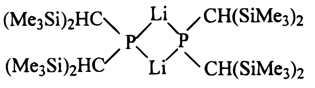
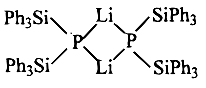


Figure 5. Stereoscopic representation of the molecular model of dimeric $LiPH_2\cdot DME$. The H atoms of the methyl and methylene groups are not shown. Reprinted with permission from ref 59. Copyright 1989 Wiley-VCH Verlag GmbH.

Solvent adducts of these types are not formed, if sufficiently bulky substituents are attached to the P atom, as was revealed by crystal structure determinations for both of the mentioned phosphanides.[53,61]





91

The solvent-free $[Li\{\mu\text{-}P(SiPh_3)_2\}_2]_2$ (**91**) (Figure 6) furnished a dimer, whereas the corresponding isopropylsilyl-substituted phosphanide $LiP(Si\textit{i}Pr_3)_2$ (**92**) is a mixed tetrameric P_4Li_4 heterocyclooctane ring bearing three molecules $LiP(Si\textit{i}Pr_3)_2$ and one molecule $LiPH(Si\textit{i}Pr_3)$ (**114**) (Figure 7). This phosphanide **114** obviously is formed by a nucleophilic cleavage of the Si−P bond in $HP(Si\textit{i}Pr_3)_2$ (**90**).[53]

The structural differences as well as the degree of oligomerization (*x*) are basically determined by the space requirement of the substituents linked to the P atom and the number of donor solvent molecules

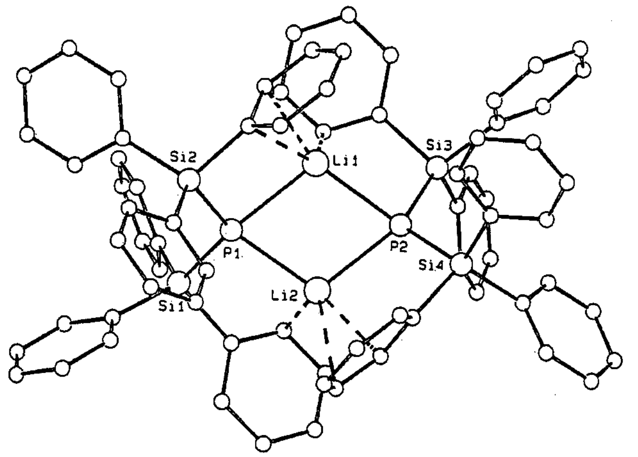


Figure 6. Molecular structure of $[Li\{\mu\text{-}P(SiPh_3)_2\}_2]_2$ (**91**). Reprinted with permission from ref 53. Copyright 1996 Wiley-VCH Verlag GmbH.

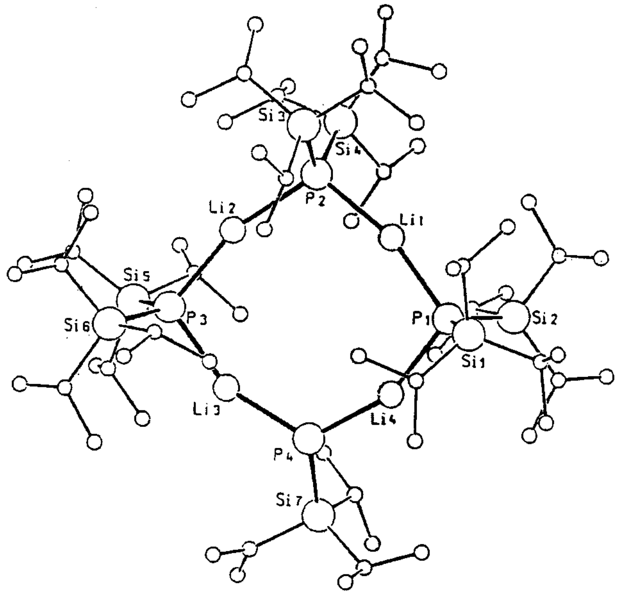
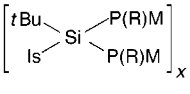


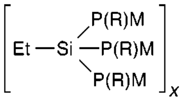
Figure 7. Molecular structure of the heterocyclooctane ring Li_4P_4. Reprinted with permission from ref 53. Copyright 1996 Wiley-VCH Verlag GmbH.

coordinated to the Li centers. Even highly functionalized molecular bis- and tris(alkali metal phosphanidyl)silanes of the types **D** and **E** follow the same building principle forming closed three-dimensional aggregates.



D

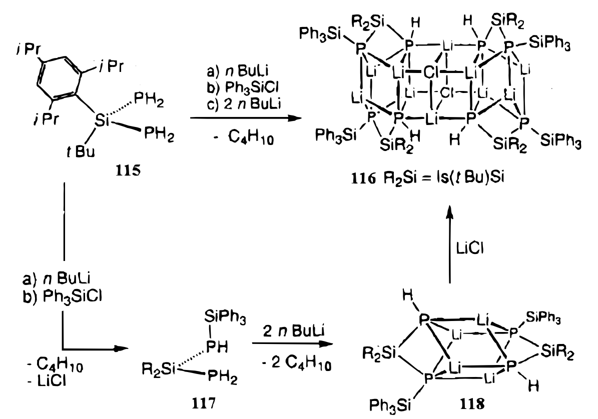
and



E

R = H, SiR_3(R = Ph, Me, *i* Pr); Is = 2, 4, 6-*i* PrC_6H_2; M = alkali metal

Scheme 1[a]



[a] Reprinted with permission from ref 66. Copyright 1995 Wiley-VCH Verlag GmbH.

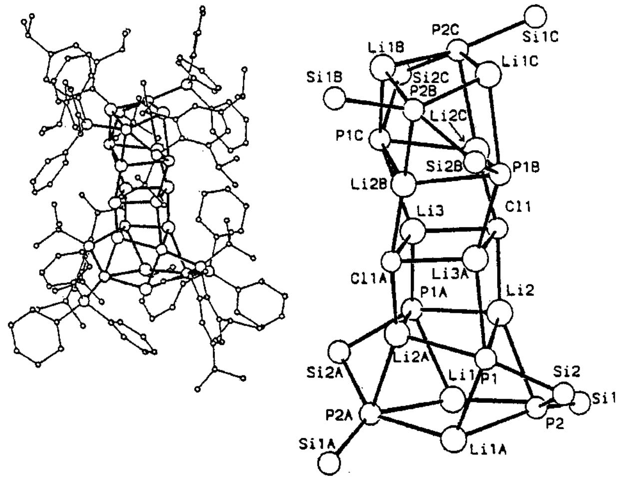
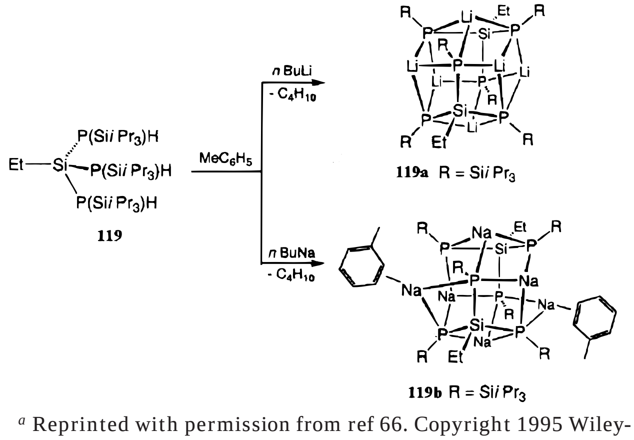


Figure 8. Molecular structure of the aggregate **116**: (right) Skeleton without organic groups. Reprinted with permission from ref 66. Copyright 1995 Wiley-VCH Verlag GmbH.

Scheme 2[a]



[a] Reprinted with permission from ref 66. Copyright 1995 Wiley-VCH Verlag GmbH.

The dimeric bis(lithiumphosphanidyl)silane **118** is accessible as colorless crystals (87%) in a one pot reaction, as illustrated in Scheme 1 by treating the bulky silylphosphane **117** with *n*BuLi.[66] Compound **118** reacts with LiCl to form the poorly soluble aggregate **116**, which has the shape of colorless rhombs (55%). In **116** two of the cluster molecules **118** are linked by a $(LiCl)_2$ unit. The P atoms are 5- and 6-fold-coordinated, whereas the Li centers have a distorted tetrahedral environment. The Cl centers in the $(LiCl)_2$ middle part show a quasi-trigonal-bipyramidal coordination. The Li1 centers are each η^2-coordinated to one Ph group of the $SiPh_3$ substituents (Figure 8). Probably this interaction and the sterical demand of the $SiPh_3$ group prevent any higher aggregation under addition of LiCl and **118**.[66]

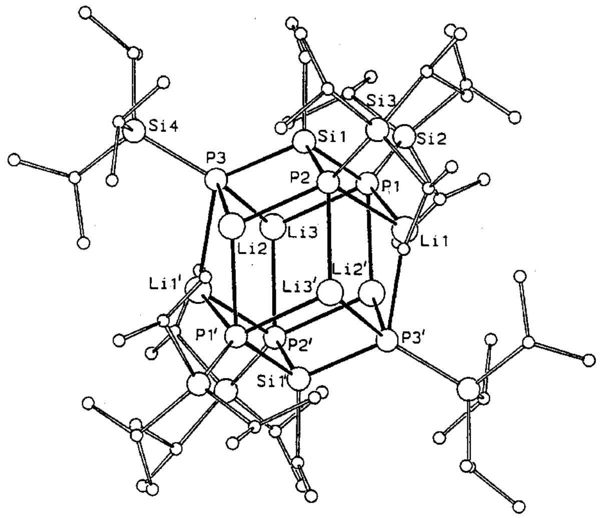


Figure 9. Molecular structure of the lithium compound **119a**. Reprinted with permission from ref 66. Copyright 1995 Wiley-VCH Verlag GmbH.

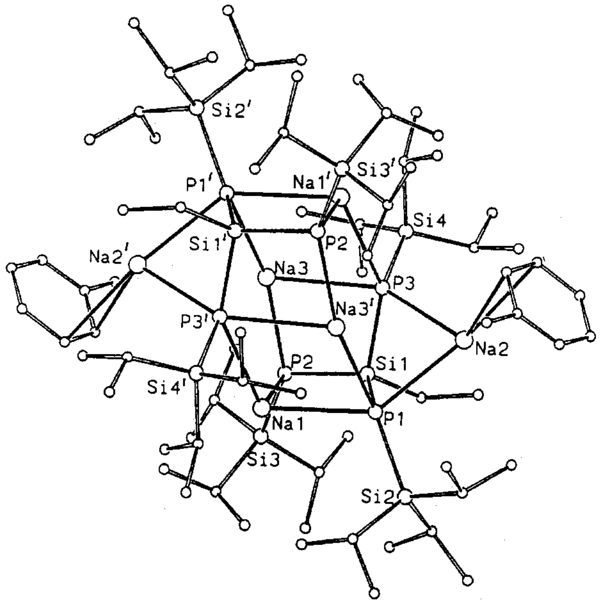


Figure 10. Molecular structure of the sodium compound **119b**. Reprinted with permission from ref 66. Copyright 1995 Wiley-VCH Verlag GmbH.

The colorlessly crystallizing compounds **119a** and **119b** were synthesized by metalation of EtSi-[P(Si*i*Pr$_3$)H]$_3$ (**119**) with *n*BuLi or *n*BuNa at −30 °C in toluene (Scheme 2).

In a one pot reaction, **119** is readily accessible by lithiating EtSi(PH$_2$)$_3$ (**28**)^{44} with LiN(*i*Pr)$_2$ (LDA) in a molar ratio of 1:3 in THF at −80 °C and substituting the phosphanide with 3 equiv of *i*Pr$_3$SiOSiO$_2$CF$_3$. As found by X-ray structure determination, **119a** consists of a solvent-free Si$_2$P$_6$Li$_6$ framework in the shape of a distorted rhombic dodecahedron (Figure 9). Although both compounds were prepared under the same conditions, **119b** crystallizing with two molecules of toluene shows a Si$_2$P$_6$Na$_6$ framework with a open polyhedron structure (Figure 10).^{66} The structures of **119a** and of the homologous tris(lithioarsino)germanes are of the same type.^{67}

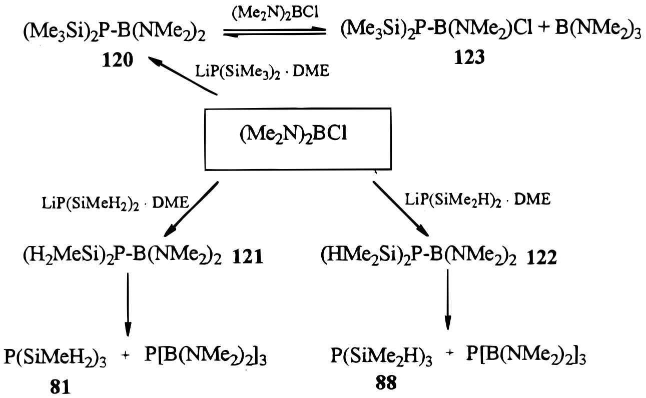
VII. Syntheses with LiP(SiMe$_3$)$_2$

The silylphosphanides MP(SiMe$_3$)$_2$ are very suitable to link the P(SiMe$_3$)$_2$ group to a great variety of halogenated B, C, and Si compounds. With halogenated phosphanes, silylated diphosphanes result which are alternatively accessible by syntheses employing Si−P bond cleavages. These are, moreover, the key reactions for the preparation of partly silylated di-, tri-, n-tetra-, isotetra-, isopenta, and hexaphosphanes.

A. Silylphosphinoboranes

Silylated lithium phosphanides such as LiP(SiMe$_3$)$_2$ (**80**) with BCl-containing aminoboranes give P-silylated boron−nitrogen compounds in good yields. In Scheme 3 the reactions of (Me$_2$N)$_2$BCl with silylated lithium-phosphanides are shown.

Scheme 3

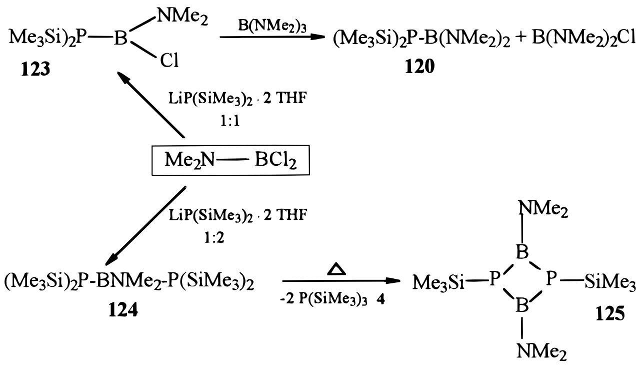


The syntheses were performed in cyclohexane or pentane, respectively. The monomeric **120** is a clear liquid and contains some **123**, resulting from the reaction of **120** with (Me$_2$N)$_2$BCl. LiP(SiMe$_3$)$_2$ (**80**) does not react with **120**. With an excess of (Me$_2$N)$_2$BCl the pure compound **120** reacts only until the equilibrium is established. By treating (Me$_2$N)$_2$BCl with LiP(SiMeH$_2$)$_2$ (**78**) at 20 °C, the colorless compound **121** is accessible which decomposes after some hours to form P[B(NMe$_2$)$_2$]$_3$ and the trisilylphosphane **81.** The reaction of LiP(SiMe$_2$H)$_2$ (**79**) with (Me$_2$N)$_2$BCl results in compound **122**, which also decomposes to P[B(NMe$_2$)$_2$]$_3$ and **88**. After removing the trisilylphosphanes, colorless crystals of the monomeric compound P[B(NMe$_2$)$_2$]$_3$ can be isolated by sublimation. Compound P(SiH$_3$)$_3$ (**5**) was obtained in addition to a yellow polymer in the reaction of LiP(SiH$_3$)$_2$ (**77**) with (Me$_2$N)$_2$BCl.

Scheme 4 shows the reactions of **80** with the dichloroaminoborane Me$_2$N−BCl$_2$. In a molar ratio of 1:1 the monochlorinated compound **123** (monomer, liquid, 70% yield) was accessible, which can form **120** with B(NMe$_2$)$_3$. The reaction in a molar ratio of 1:2 yields compound **124** (white crystals at −20 °C from cyclopentane). The thermolysis of **124** produces **125** quantitatively in addition to **4**. The formation of the four-membered ring **125** is a typical example for a cyclization by elimination of **4**.

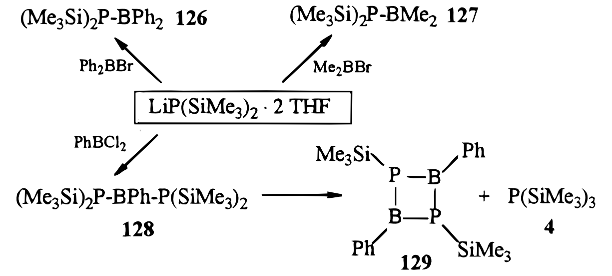
Similarly, Ph$_2$BBr reacts to (Me$_3$Si)$_2$P−BPh$_2$ (**126**), Me$_2$BBr to (Me$_3$Si)$_2$P−BMe$_2$ (**127**), and PhBCl$_2$ with 2 mol of **80** to (Me$_3$Si)$_2$P−BPh−P(SiMe$_3$)$_2$ (**128**),

Scheme 4



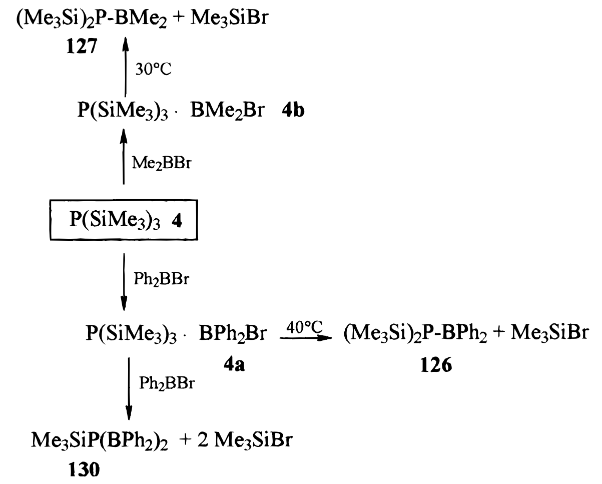
which decomposes yielding **4** and yellow crystals of the cyclic $[Me_3SiP{-}BPh]_2$ (**129)** (Scheme 5).[68]

Scheme 5



Silylphosphanes form adducts with EtJ, BCl_3, $AlCl_3$, and similar compounds which react under Si$-$P bond cleavage when heated, yielding the corresponding phosphorus-element compounds.[14-16,69] Analogously, silylphosphinoboranes are accessible from the 1:1 adducts of **4** with boron alkylhalides, as demonstrated in Scheme 6.

Scheme 6



The insoluble compound **4a** resulting from the reaction with Ph_2BBr decomposes at 40 °C to form **126** under elimination of Me_3SiBr. The crystalline compound **130** (recrystallized from pentane) was synthesized by adding Ph_2BBr to **4a**. Analogously, **127** can be prepared by treating **4** with Me_2BBr via the adduct **4b**. At 20 °C **4** and $(Me_2N)_2BCl$ do not form a stable adduct, and even after heating for several days at 90 °C, no **120** could be obtained.[68]

Further phosphanylboranes can be synthesized as shown in (75). Initially monomers are obtained which, however, form dimers of the composition $[R(X)B{-}PR'SiMe_3]_2$, depending on their substituents.

$$RBX_2 + LiPR'(SiMe_3) \rightarrow R(X)B{-}PR'(SiMe_3) + LiX \quad (75)$$

In Table 6 both types of compounds with their NMR data are summarized.

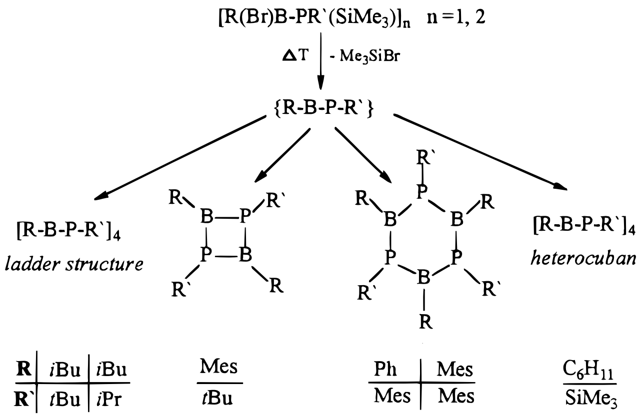
In the hydrolysis of the dimeric phosphanylboranes neither the boron$-$halogen nor the boron$-$phosphorus bond is attacked; instead the Si$-$P bond is cleaved, and PH-containing dimers are observed according to (76).

$$[R_2B\text{-}PtBu(SiMe_3)]_2 \xrightarrow{OH^-} [R_2B{-}PtBuH]_2$$
$$R_2 = Cl_2\ (\mathbf{132}),\ Br_2\ (\mathbf{133}),\ I_2\ (\mathbf{134}),\ C_6H_{11}(Br)\ (\mathbf{137}) + (Me_3Si)_2O$$

$$\underset{\mathbf{150}}{[tBu(Br)B{-}PiPr(SiMe_3)]_2} \xrightarrow{OH^-} [tBu(Br)B{-}PiBrH]_2 + (Me_3Si)_2O \quad (76)$$

The influence of the substituents on the stabilizing reactions of phosphanylboranes $[R(Br)B{-}PR'(SiMe_3)]_n$ ($n = 1, 2$) after elimination of Me_3SiBr is summarized by selected examples in Scheme 7. The formed tetrameres $[R{-}B{-}P{-}R']_4$ can adopt either a heterocubane or a ladder structure. If the starting compound has the substituents R = *i*Bu, R′ = *t*Bu or *i*Pr, a ladder structure is realized, a novel structural type in boron$-$phosphorus chemistry.

Scheme 7



Diphosphanylboranes $RB[PR'(SiMe_3)]_2$ can be prepared as demonstrated in (77) and (78). The NMR data are shown in Table 7.

$$RBX_2 + 2LiPR'(SiMe_3) \rightarrow RB[PR'(SiMe_3)]_2 + 2LiX \quad (77)$$

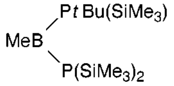
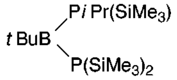
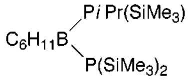
$$R(X)B{-}PR'(SiMe_3) + LiPR'(SiMe_3) \rightarrow RB[PR'(SiMe_3)]_2 + LiX \quad (78)$$

B$-$P heterocubanes are accessible from diphosphanylboranes, either by elimination of **4** from $C_6H_{11}B$-

Table 6. NMR Data of the Monomeric $R_2B{-}PR'(SiMe_3)$ and Dimeric $[R_2B{-}PR'(SiMe_3)]_2$ Phosphanylboranes

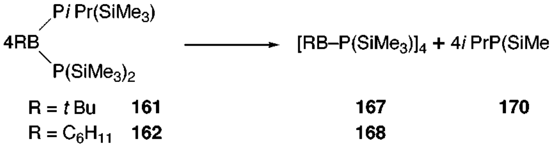
R_2		$\delta(^{11}B)$ (ppm)	$\delta(^{31}P)$ (ppm)	^{29}Si (ppm)
$[R_2B{-}PtBu(SiMe_3)]_2$				
HBr	**131**	−19.0 (117)	cis −56.4 trans −60.1	
Cl_2	**132**	1.13 (82.3) 0.93 (82.9)	−26.5 −27.4	13.0 (24.3) 13.3 (22.4)
Br_2	**133**	−10.4 (78.0)	−31.6	17.1 (13.1)
I_2	**134**	−46.9 (68.8)	−40.4	
MeBr	**135**	−3.5	−31.4 −37.2	
*i*BuBr	**136**	−1.4	−32.4 −34.8	9.3 (16.7) 9.5 (14.3)
$C_6H_{11}(Br)$	**137**	4.0	−39.3	
$R_2B{-}PtBu(SiMe_3)$				
*t*BuCl	**138**	84.5	−56.8	1.25
*t*BuBr	**139**	85.9	−48.6	1.02
MesBr	**140**	69.0 67.6	−4.5 −2.1	4.5 (3.5) 3.4 (8.2)
$[R_2BP(SiMe_3)_2]_2$				
MeBr	**141**	−5.16	−122.9	cis 6.3 (3.0), 13.2 (18.3) trans 9.6 (15.8)
$[iBuBrB{-}P(SiMe_3)]_2$ ⇅	**142**	−2.0 −1.3; −3.3	−118.5	9.2 (15.8)
$2iBu(Br)B{-}P(SiMe_3)_2$	**143**	76.0	−116.0	
$[tBuBrB{-}P(SiMe_3)]_2$ ⇅	**144**	trans 2.7 cis 6.9	−107.4 −141.9	10.6 9.7
$2tBu(Br)B{-}P(SiMe_3)_2$	**145**	82.8	−141.1	4.9
$C_6H_{11}Br$	**146**	2.0	−130.6	9.0 (8.2)
$R_2B{-}P(SiMe_3)_2$				
*t*BuCl	**147**	81.1	−156.0	4.4
MesBr	**148**	72.4	−110.6	6.2 (7.3) 5.0 (2.2)
$[R_2B{-}PiPr(SiMe_3)]_2$				
*i*BuBr	**149**	−2.8	−56.0	7.1
*t*BuBr	**150**	5.5	−41.4	9.1 (30.4)
$C_6H_{11}(Br)$	**151**	1.1 1.0	−53.9 −53.2	8.9 (34.3) 11.0 (35.7)

Table 7. NMR Data of the Diphosphanylboranes $RB[PR'(SiMe_3)]_2$

compd		$\delta(^{11}B)$ (ppm)	$\delta(^{31}P)$ (ppm)	$\delta(^{29}Si)$ (ppm)
$MeB[PtBu(SiMe_3)]_2$	**152**	91.7	−34.5	0.4 (7.9)
$MeB[P(SiMe_3)_2]_2$	**153**	92.1	−139.6	
$tBuB[P(tBu)SiMe_3]_2$	**154**	77.7	−33.7	1.2 (38.4)
$HB[P(tBu)_2]_2$	**155**	55.1	57.2	
$C_6H_{11}B[P(tBu)_2]_2$	**156**	76.5	51.6	
$C_6H_{11}B[PtBu(SiMe_3)]_2$	**157**	82.9	−32.9	1.2 (11.2)
$C_6H_{11}B[P(SiMe_3)_2]_2$	**158**	yields cubane		
$C_6H_5B[P(SiMe_3)_2]_2$	**159**	86.3	−127.4	2.8
	**160**	92.2	−29.7 (84.0)	−150.4 (84.0)
	**161**		−37.7	−141.5
	**162**	83.8	−25.6 (121.5) −163.0 (121.5)	

[P(SiMe₃)]₂ (**158**) according to (79), or to (80). There no elimination of **4** occurs.

$$\underset{\mathbf{158}}{4C_6H_{11}B[P(SiMe_3)_2]_2} \longrightarrow \underset{\mathbf{168}}{[C_6H_{11}B{-}PSiMe_3]_4} + \underset{\mathbf{4}}{4P(SiMe_3)_3} \qquad (79)$$



(80)

The NMR data of the B−P heterocubanes synthesized following this pathway are shown in Table 8. Results of X-ray crystallographic studies have been given for compounds **161**−**166**.[70]

Table 8. NMR Data of the Boron and Phosphorus Heterocubanes

compd		$\delta(^{11}B)$ (ppm)	$\delta(^{31}P)$ (ppm)	$\delta(^{29}Si)$ (ppm)
$[MeB{-}PtBu]_4$	**163**	−0.252 “Qui”	−21.8	
$[ClB{-}PtBu]_4$	**164**	−0.55 (66.7)	−7.2 (66.2)	
$[BrB{-}PtBu]_4$	**165**	−5.90 (66.8)	−25.1	
$[IB{-}PtBu]_4$	**166**	−20.81 (65.2)	−53.0	
$[tBuB{-}PSiMe_3]_4$	**167**	1.37	−96.4	0.76
$[C_6H_{11}B{-}PSiMe_3]_4$	**168**	−1.62	100.2	
$[C_6H_{11}B{-}PtBu]_4$	**169**	−5.96 (66.8)	−30.7	

Figure 11 shows the structure of $[C_6H_{11}B{-}PSiMe_3]_4$ (**168**).

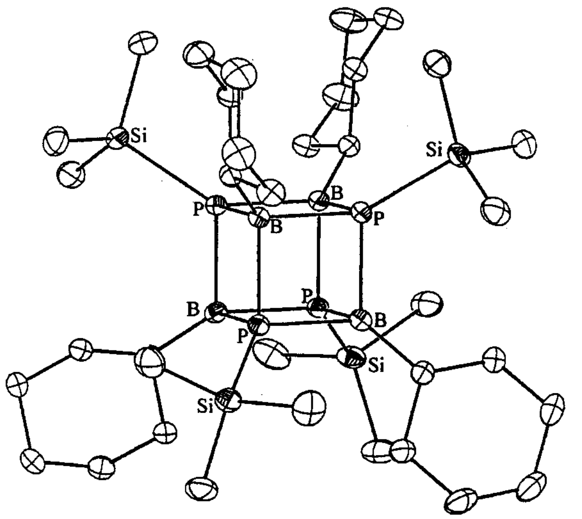


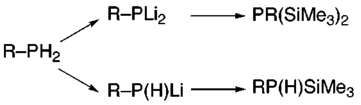
Figure 11. Molecular structure of $[C_6H_{11}B-PSiMe_3]_4$ (**168**). Reprinted with personal permission from ref 70.

B. Reactions of Chlorinated Hydrocarbons with $LiP(SiMe_3)_2$

The easy transfer of the $P(SiMe_3)_2$ group by means of $LiP(SiMe_3)_2$ is also suitable for the formation of bis(silyl)phosphanes starting from chlorinated hydrocarbons, as several examples show in Scheme 8.

By adding CH_3Cl to a cooled solution of the lithium phosphanide in cyclopentane, compound **171** was obtained. The corresponding reaction with CH_2Cl_2 in a molar ratio of 2:1 at 20 °C yields compound **172** with a small amount of **4**. The analogous reaction in a molar ratio of 1:1 does not result in $(Me_3Si)_2P-CH_2-Cl$; rather the formation of **172** is observed again. However 1,2-dichloroethane forms compound **173** (yield 60%) at 20 °C, and in a molar ratio of 2:1 it gives **174** (ca. 35%) in addition to **4** (ca. 26%). From $C_6H_5CH_2Cl$ the water clear benzylbis(trimethylsilyl)phosphane (**175**) is accessible in 88% yield.[71] In an analogous manner $(Me_3Si)_2P-CH(C_6H_5)_2$ (**176**) was formed.[72]

Alkyl- and arylbis(trimethylsilyl)phosphanes, $RP(SiMe_3)_2$, can also be obtained from the corresponding phosphanes RPH_2 with alkyl- or aryl-substituted alkali metal phosphanides and halogenosilanes, as demonstrated in (81).



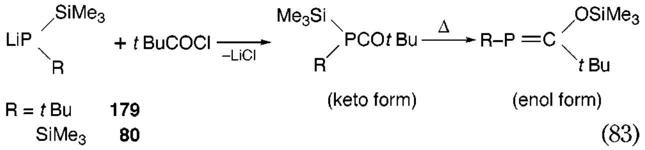
(81)

The necessary primary phosphanes RPH_2 (R = Me, Ph, *t*Bu, Cy, Mes) were prepared from the functional alkyl- or arylphosphanes (functional groups: $P-Cl_2$, $-P(O)Cl_2$, $-P(O)(OMe)_2$) by reduction with $LiAlH_4$.

The reaction of $PhP(SiMe_3)_2$ (**177**) with water leads to **178** by cleavage of a Si–P bond according to (82).

$$\underset{\mathbf{177}}{PhP(SiMe_3)_2} + H_2O \rightarrow \underset{\mathbf{178}}{PhP(H)SiMe_3} + Me_3SiOH \qquad (82)$$

Both initial reaction products react on to give $PhPH_2$ and $(Me_3Si)_2O$. For this reason compound **178** can be isolated in an amount of 73% only if **177** is used in excess (1:0.5 H_2O). The reaction of $LiP(R)SiMe_3$ with the carboxylic acid halogenide *t*Bu–CO–Cl gives the keto product, but 1,3-migration of the $SiMe_3$ group from phosphorus to oxygen yielding the enol form takes place at increased temperature, as demonstrated in (83).[72]



(83)

$MeP(SiPh_3)_2$ (**180**) is accessible according to (84). Nevertheless, this reaction did not gain widespread preparative importance.[73]

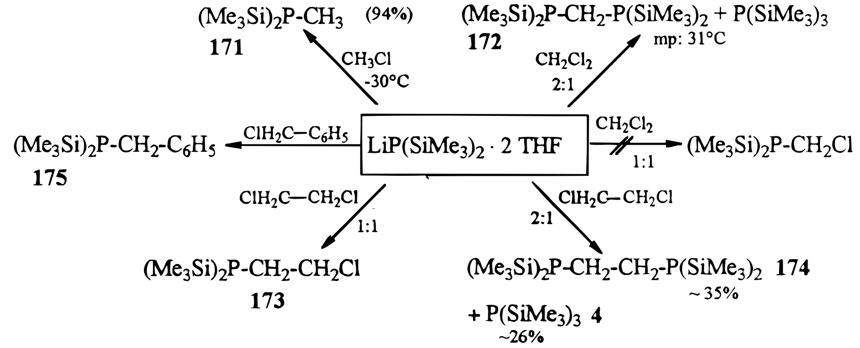
$$2LiSiPh_3 + MePBr_2 \rightarrow \underset{\mathbf{180}}{MeP(SiPh_3)_2} + 2LiCl \qquad (84)$$

The formation of trimethylsilylphosphanes from Me_3SiCl, PCl_3, and Mg was reported by several groups.[74]

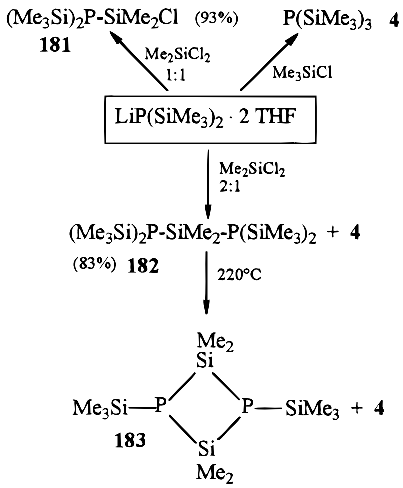
C. Reactions of Silylated Lithium Phosphanides with Dichlorosilanes

The reactions of **80** with dimethyldichlorosilane are shown in Scheme 9. Dependent on the molar ratio, two different products were obtained, $(Me_3Si)_2P-SiMe_2Cl$ (**181**; molar ratio 1:1) and $(Me_3Si)_2P-SiMe_2-P(SiMe_3)_2$ (**182**; molar ratio 2:1). Compound **181** containing one Cl atom can be purified by distillation without loss caused by Si–P cleavage. Compound **182** is difficult to separate from its byproduct **4**. While the reaction mixture (13 h) is stored at 20 °C, the amount of **4** increases. Syntheses in DME immediately give **4**. At 220 °C **182** reacts to form **183**. This

Scheme 8



Scheme 9



is a further example for a cyclization caused by elimination of P(SiMe$_3$)$_3$.[71]

D. Preparations and Reactions of Silylated Diphosphanes

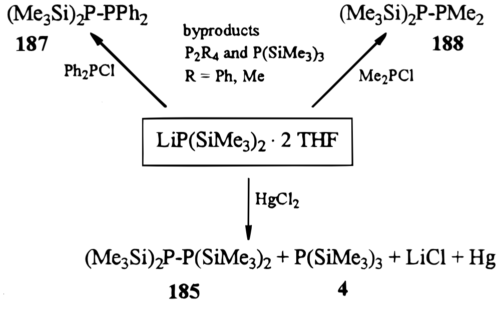
The first silylated diphosphane [(Me$_3$Si)PhP]$_2$ (**184**) was synthesized by Baudler et al., as shown in (85).[75]

$$(Me_3Si)PhPK \xrightarrow[-KX]{X_2} (Me_3Si)PhPX \xrightarrow{(Me_3Si)PhPK} \underset{\mathbf{184}}{[(Me_3Si)PhP]_2} \qquad (85)$$

Schumann and Fischer[76] reported the formation of [(Me$_3$Si)$_2$P]$_2$ (**185**) and **184**, Hengge et al.[77] published the synthesis of the four-membered ring [(Me$_2$Si)–PPh]$_2$ (**186**) with Si–Si and P–P bonds by treating ClMe$_2$Si–SiMe$_2$Cl with KPhP–PPhK.

Reactions of **80** with monochlorinated phosphanes R$_2$PCl (R = Ph, Me) lead to the diphosphanes (Me$_3$Si)$_2$P–PPh$_2$ (**187**) or (Me$_3$Si)$_2$P–PMe$_2$ (**188**), respectively (Scheme 10).[71] With HgCl$_2$ the tetrakis(trimethylsilyl)diphosphane **185** was obtained.[78]

Scheme 10



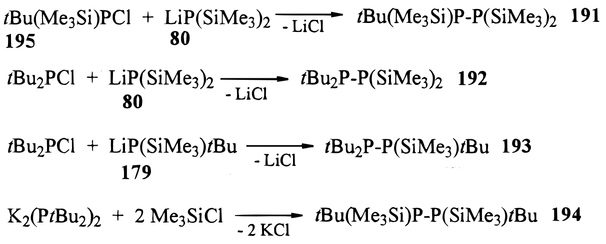
As Si–P bonds are cleaved by chlorophosphanes, the syntheses and reactions of higher functional derivatives turn out to proceed by various pathways. The reaction of **4** with 3 mol of Ph$_2$PCl was reported to yield P(PPh$_2$)$_3$, while red phosphorus was obtained with 3 mol of PCl$_3$.[79] By treating **177** with Ph$_2$PCl or *t*BuPhPCl, the disilylphosphanes Ph$_2$P–P(SiMe$_3$)Ph (**189**) or *t*BuPhP–P(SiMe$_3$)Ph (**190**), respectively, were accessible.[74e]

The reaction as demonstrated in (86) yields **187** and **188** by Si–P bond cleavage. Both product mixtures still contain **4** and R$_2$P–PR$_2$. The formation of these side products is explained by the disproportionation of unsymmetrical substituted diphosphanes.[71]

$$\underset{\mathbf{4}}{P(SiMe_3)_3} + R_2PCl \xrightarrow[-Me_3SiCl]{} \begin{array}{l}(Me_3Si)_2P-PR_2\\ R = Ph\ (\mathbf{187})\\ R = Me\ (\mathbf{188})\end{array} \qquad (86)$$

As described elsewhere,[80] the silylated diphosphanes **191**–**194** (Scheme 11) were obtained from suitable substituted functional phosphanes.[81,82]

Scheme 11



The Si–P bonds in **191**–**194** can be cleaved by CH$_3$OH in a molar ratio of 1:1 in toluene under formation of Me$_3$SiOMe to prepare the respective PH-containing derivatives **196**–**199**. With BuLi in THF/hexane solution the diphosphanes **191**–**194** yield the lithium phosphanides **200**–**203** (formation of BuSiMe$_3$) (Scheme 12).[80]

*t*Bu(H)P–P(H)*t*Bu is accessible by hydrolysis of K$_2$(P*t*Bu)$_2$.[82]

E. Reactions of Functional Diphosphanes to Tri- and Tetraphosphanes

Functional diphosphanes are prepared by treating PCl-containing phosphanes with lithium phosphanides or by cleavage of silylphosphanes (87), respectively.[68,71]

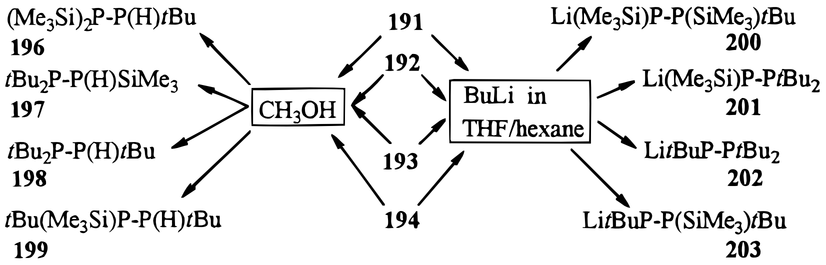
$$RP(SiMe_3)_2 + PCl_3 \xrightarrow[-Me_3SiCl]{} R(Me_3Si)P-PCl_2 \qquad (87)$$

The formation of triphosphanes requires in the next step a reaction with reactive phosphanides (88), proceeding in a one pot reaction over multistep pathways.

$$\begin{array}{l}R(Me_3Si)P-PCl_2\ +\\ \quad R = tBu\ (\mathbf{204})\\ \quad R = Me\ (\mathbf{205})\end{array} \begin{array}{l}LiP(SiMe_3)R' \xrightarrow[-LiCl]{}\\ \quad R' = SiMe_3\ (\mathbf{80})\\ \qquad = tBu\ (\mathbf{179})\end{array}$$

$$\begin{array}{r}R(Me_3Si)P-PCl-P(SiMe_3)R'\\ R = tBu,\ R' = SiMe_3\ (\mathbf{207})\\ = tBu\ (\mathbf{255})\\ R = Me,\ R' = SiMe_3\ (\mathbf{253})\\ = tBu\ (\mathbf{254})\end{array} \qquad (88)$$

Scheme 12



The dimethylated triphosphane $Me(Me_3Si)P{-}PCl{-}P(SiMe_3)Me$ (**252**) was not available in this way. It could be synthesized according to (88) using a 2:1 molar ratio of the reactants.

Such triphosphanes, containing both PCl and $PSiMe_3$ groups, decompose at room temperature by elimination of Me_3SiCl. A stabilization with *t*BuLi at −78 °C leads via the phosphanides (89) to the protonated triphosphanes (90).

$$R(Me_3Si)P{-}PCl{-}P(SiMe_3)R' \xrightarrow[-t\text{BuCl}]{+t\text{BuLi}} R(Me_3Si)P{-}PLi{-}P(SiMe_3)R' \quad (89)$$

$$\begin{aligned} R &= t\text{Bu}, R' = SiMe_3\ (\mathbf{208}) \\ &\phantom{= t\text{Bu}, R'} = t\text{Bu}\ (\mathbf{231}) \\ R &= \text{Me}, R' = SiMe_3\ (\mathbf{253a}) \\ &\phantom{= \text{Me}, R'} = t\text{Bu}\ (\mathbf{254b}) \end{aligned}$$

$$R(Me_3Si)P{-}PLi{-}P(SiMe_3)R' \xrightarrow[\substack{-\text{LiCl} \\ -Me_2C{=}CH_2}]{+t\text{BuCl}} R(Me_3Si)P{-}PH{-}P(SiMe_3)R' \quad (90)$$

$$\begin{aligned} R &= t\text{Bu}, R' = SiMe_3\ (\mathbf{209}) \\ &\phantom{= t\text{Bu}, R'} = t\text{Bu}\ (\mathbf{301}) \\ R &= \text{Me}, R' = SiMe_3\ (\mathbf{253b}) \\ &\phantom{= \text{Me}, R'} = t\text{Bu}\ (\mathbf{254b}) \end{aligned}$$

These PH-containing representatives can be isolated by fractionated sublimation. The desired silylated triphosphanides are available by another metalation with BuLi (91). Because of their poor solubility in nonpolar solvents, they can be isolated very easily.[83]

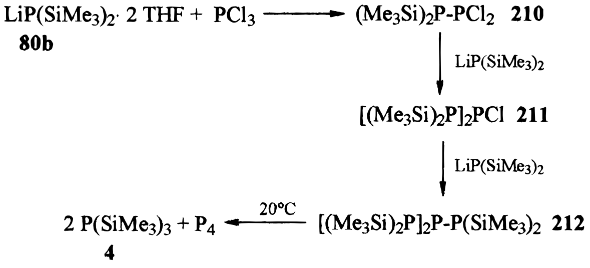
$$R(Me_3Si)P{-}PH{-}P(SiMe_3)R' \xrightarrow[-\text{BuH}]{+\text{BuLi}} R(Me_3Si)P{-}PLi{-}P(SiMe_3)R' \quad (91)$$

In the (89) analogous metalation of $Me(Me_3Si)P{-}PCl{-}P(SiMe_3)Me$ (**252**), substitution of the chlorine on the secondary P atom by the *t*Bu group was observed.

Reactions between $LiP(SiMe_3)_2$ and PCl_3 give an insight into the synthetic possibilities and the reactions of functional diphoshanes with P−Si and P−Cl groups. The products of these reactions are summarized in Scheme 13.

At −78 °C in a first step $(Me_3Si)_2P{-}PCl_2$ (**210**) is formed, followed by the triphosphane **211**, which still contains one PCl group, and in the next step the completely silylated isotetraphosphane **212** is obtained, which decomposes at 20 °C, yielding **4** and P_4.[84] For syntheses of P-rich silylphosphanes with different functional groups it turned out to be suitable to start the reaction between $LiP(SiMe_3)_2$ and PCl_3 at −78 °C and to add then *t*BuLi. In this way one P−Cl group was transferred into the nearly inert P−*t*Bu group (92).

Scheme 13



$$\underset{\mathbf{210}}{(Me_3Si)_2P{-}PCl_2} + t\text{BuLi} \rightarrow \underset{\mathbf{213}}{(Me_3Si)_2P{-}P(Cl)t\text{Bu}} + \text{LiCl} \quad (92)$$

Compound **213** is capable of undergoing a Li/Cl replacement (93), which is followed by an attack of the also formed *t*BuCl to yield the PH-containing diphosphane **196** (94).

$$\underset{\mathbf{213}}{(Me_3Si)_2P{-}P(Cl)t\text{Bu}} + t\text{BuLi} \rightarrow \underset{\mathbf{214}}{(Me_3Si)_2P{-}P(Li)t\text{Bu}} + t\text{BuCl} \quad (93)$$

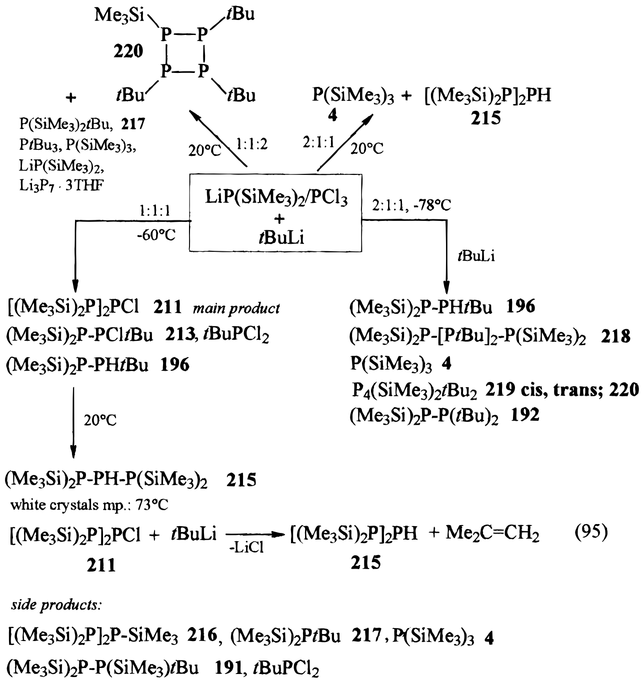
$$\mathbf{214} + t\text{BuCl} \rightarrow \underset{\mathbf{196}}{(Me_3Si)_2P{-}P(H)t\text{Bu}} + Me_2C{=}CH_2 + \text{LiCl} \quad (94)$$

A choice in favor of specific reaction products is possible by selecting suitable molar ratios of the reactants even in a one pot synthesis (Scheme 14).

The reaction of PCl_3 with **80** generally starts at −78 °C. After 8 h at this temperature *t*BuLi was added and after 6 h the mixture warmed to 20 °C. Using a molar ratio of 1:1:1 at −78 °C the triphosphane **211** is the main product in the reaction mixture in addition to **213** and **196**, both resulting from substitutions by *t*BuLi. After warming to 20 °C, the triphosphane **215** is obtained as the major product (eq 95 in Scheme 14). Among the minor products $[(Me_3Si)_2P]_2P{-}SiMe_3$ (**216**) and **191** result from the silylation of **211** and **213**, respectively.

By running the reaction in a molar ratio of 2:1:1 at −78 °C and adding *t*BuLi only after 24 h, ad-

Scheme 14



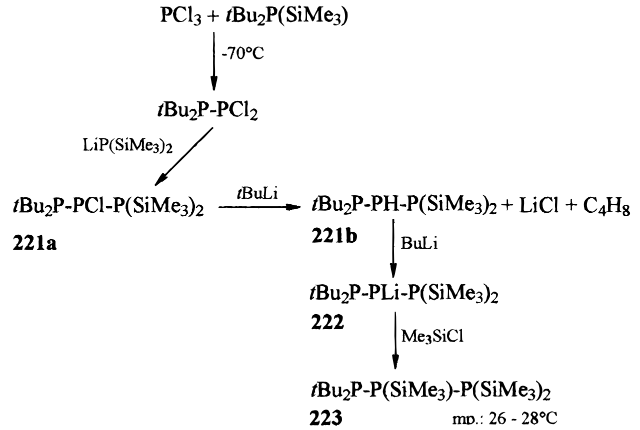
ditionally to **196** and **4**, tetraphosphane **218** is obtained, which is formed as demonstrated in (96).

$$\underset{\mathbf{213}}{(\mathrm{Me_3Si})_2\mathrm{P{-}P(Cl)}t\mathrm{Bu}} + \underset{\mathbf{214}}{(\mathrm{Me_3Si})_2\mathrm{P{-}P(Li)}t\mathrm{Bu}} \xrightarrow[-\mathrm{LiCl}]{} \underset{\mathbf{218}}{(\mathrm{Me_3Si})_2\mathrm{P{-}[P}t\mathrm{Bu}]_2\mathrm{{-}P(SiMe_3)_2}} \quad (96)$$

The formation of **4** corresponds to the behavior of high-silylated di- and triphosphanes. The cyclotetraphosphane **220** and additionally P(tBu)$_3$ were obtained by running the reaction with an excess of tBuLi (1:1:2) and warming the mixture to 20 °C in addition to **4**, Li$_3$P$_7$, and **80**, which result from the highly silylated phosphanes formed initially before adding tBuLi. With an inverted molar ratio (2:1:1), **4** is the main product in addition to triphosphane **215**.

Starting from PCl$_3$, silylated di- and triphosphanes are accessible via Si−P cleavage, as demonstrated by the reaction of PCl$_3$ with P(SiMe$_3$)$_3$ (97) and tBu$_2$P(SiMe$_3$) (Scheme 15) at −78 °C.

Scheme 15



$$\underset{\mathbf{4}}{\mathrm{P(SiMe_3)_3}} + \mathrm{PCl_3} \rightarrow \underset{\mathbf{210}}{(\mathrm{Me_3Si})_2\mathrm{P{-}PCl_2}} + \mathrm{Me_3SiCl} \quad (97)$$

Even after warming the reaction mixture to 10 °C, no new signals were observed in the ^{31}P NMR spectrum. However, further warming leads to decomposition.

$$\underset{\mathbf{210}}{(\mathrm{Me_3Si})_2\mathrm{P{-}PCl_2}} \rightarrow 2\mathrm{P_4} + 2\mathrm{Me_3SiCl} \quad (98)$$

By starting the reaction according to (97) and then adding tBuLi in different molar ratios (1:1:1, 1:1:2, and 1:1:3), generally the same compounds as already described in Scheme 14 were obtained.[84]

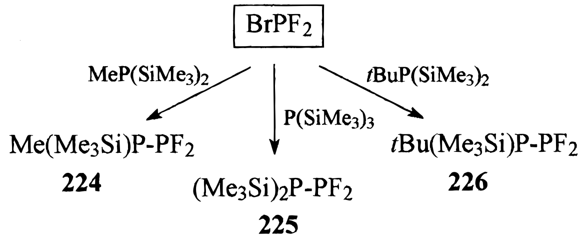
In Scheme 15 the products of the reaction between PCl$_3$ and tBu$_2$P(SiMe$_3$) and of the following secondary reactions are reported.

By eliminating a silyl group, the diphosphane tBu$_2$P−PCl$_2$ is formed, which then with LiP(SiMe$_3$)$_2$ (**80**) gives the PCl-containing triphosphane **221a**, and, after reacting with tBuLi, eventually yields the PH-containing derivative **221b**. Lithiation in nonpolar solvents resulted without Si−P cleavage in the lithiumphosphanide **222**, which reacts with Me$_3$SiCl to the triphosphane **223**.[85] In an analogous manner, e.g., with tBuP(SiMe$_3$)$_2$ (**217**), silylated triphosphanes with a different pattern of tBu groups are accessible.[83]

1. Formations and Reactions of P-Fluorinated and P-Silylated Di- and Triphosphanes

Whereas PF$_3$ with silylated phosphanes does not yield PF$_2$-containing diphosphanes, these products were formed from BrPF$_2$ by Si−P bond cleavage as the reactions in Scheme 16 show.

Scheme 16



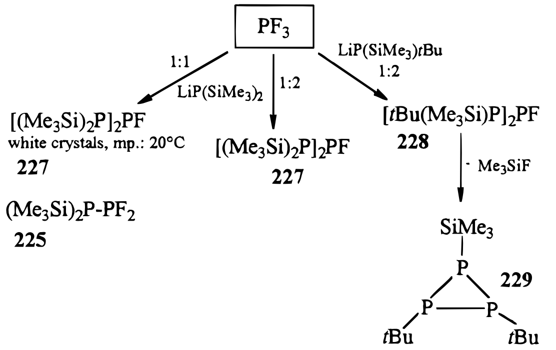
The fluorinated diphosphanes **224**−**226** are liquids at 20 °C and decompose slowly, but are considerably more stable than the corresponding chlorine derivatives.

Scheme 17 shows the reactions of PF$_3$ with **80** and LiP(SiMe$_3$)tBu (**179**), respectively, in different molar ratios, producing fluorinated and silylated triphosphanes.

The lithiated diphosphane LitBuP−P(SiMe$_3$)tBu (**203**) reacts with BrPF$_2$ as well as with PF$_3$ to form tBu(Me$_3$Si)P−PtBu−PF$_2$ (**230**), which however cannot be obtained directly from tBu(Me$_3$Si)P−P(SiMe$_3$)-tBu (**194**) and BrPF$_2$. The reaction of PF$_3$ with LiP[P(SiMe$_3$)tBu]$_2$ (**231**) leads quantitatively to the isotetraphosphane [tBu(Me$_3$Si)P]$_2$P−PF$_2$ (**232**).

These PF-substituted and silylated di- and triphosphanes are more stable than the corresponding

Scheme 17



chlorine derivatives, but there are significant differences in their reaction behavior. Whereas compounds containing a PCl group react with *t*BuLi by transmetalation to lithium phosphanides or PH-containing derivatives, respectively, in PF-containing phosphanes a P−P cleavage occurs first according to (99).[86]

$$\underset{\textbf{233}}{(\mathrm{Me_3Si})_2\mathrm{P{-}P(F)}t\mathrm{Bu}} \xrightarrow{+t\mathrm{BuLi}} (\mathrm{tBu})_2\mathrm{PF} + \underset{\textbf{80}}{\mathrm{LiP(SiMe_3)_2}} \xrightarrow[-\mathrm{LiF}]{} \underset{\textbf{192}}{t\mathrm{Bu_2P{-}P(SiMe_3)_2}} \quad (99)$$

2. Silylated Triphosphanes

The synthesis of silylated triphosphanes uses as starting reaction the treatment of PCl-containing phosphanes with silylated lithium phosphanides or the reaction of a silylated phosphane with a chlorophosphane via cleavage of a Si−P bond, as demonstrated in Schemes 10 and 15. In one pot reactions with appropriate molar ratios, step by step the triphosphanes with $\mathrm{P(SiMe_3)_2}$, $\mathrm{P(SiMe_3)}t\mathrm{Bu}$, and $\mathrm{P(SiMe_3)Me}$ groups at the primary P atom and Cl, H, Li, $\mathrm{SiMe_3}$, or *t*Bu groups at the secondary P atom are accessible.

For the preparation of silylated triphosphanes with several *t*Bu groups at different P atoms, reactions of diphosphanides such as $\mathrm{Li(Me_3Si)P{-}P(SiMe_3)}t\mathrm{Bu}$ (**200**), $\mathrm{Li(Me_3Si)P{-}P}t\mathrm{Bu_2}$ (**201**), and $\mathrm{Li(}t\mathrm{Bu)P{-}P(SiMe_3)}t\mathrm{Bu}$ (**203**) with chlorophosphanes such as $\mathrm{P(SiMe_3)}t\mathrm{BuCl}$ (**195**), $\mathrm{P}t\mathrm{Bu_2Cl}$, and $\mathrm{P}t\mathrm{BuCl_2}$ are suitable, yielding the triphosphanes $[t\mathrm{Bu(Me_3Si)P}]_2\mathrm{P{-}SiMe_3}$ (**234**), $t\mathrm{Bu(Me_3Si)P{-}P(SiMe_3){-}P}t\mathrm{Bu_2}$ (**235**), $[t\mathrm{Bu_2P}]_2\mathrm{P{-}SiMe_3}$ (**236**), and $t\mathrm{Bu(Me_3Si)P{-}P(SiMe_3){-}P}t\mathrm{Bu(Cl)}$ (**237**).[85]

3. Silylated n-Tetraphosphanes

Silylated triphosphanes are not suitable for the formation of functional, linear higher homologues, because the cyclization is favored, which proceeds in PCl-substituted compounds by elimination of $\mathrm{Me_3SiCl}$ and in $\mathrm{PSiMe_3}$-containing derivatives by formation of $\mathrm{P(SiMe_3)_3}$. In the silylated cyclotetraphosphanes $\mathrm{P_4(SiMe_3)_4}$ (**238**), *cis*-$\mathrm{P_4(SiMe_3)_2}t\mathrm{Bu_2}$ (**219**), and $\mathrm{P_4(SiMe_3)_3}t\mathrm{Bu}$ (**239**) the ring is cleaved by BuLi, leading to the corresponding lithium tetraphosphanides.[87]

The first silylated tetraphosphane $t\mathrm{Bu(Me_3Si)P{-}(P}t\mathrm{Bu)_2{-}P(SiMe_3)}t\mathrm{Bu}$ (**240**) was accessible by treating the cyclophosphane $\mathrm{P_4}t\mathrm{Bu_4}$ with potassium in THF to form first $\mathrm{K(}t\mathrm{Bu)P{-}(P}t\mathrm{Bu)_2{-}P(}t\mathrm{Bu)K}$,[88a] which reacts further with $\mathrm{Me_3SiCl}$ to **240**.[88b] After stable derivatives of diphosphanes such as $t\mathrm{Bu(Me_3Si)P{-}P(SiMe_3)Li}$ (**200**) and the *t*Bu-substituted analogous $t\mathrm{Bu_2P{-}P(SiMe_3)Li}$ (**201**) or $t\mathrm{Bu(Me_3Si)P{-}P}t\mathrm{BuLi}$ (**203**) were available,[80] the synthesis of the following silylated *n*-tetraphosphanes by reaction with 1,2-dibromoethane was developed.

$t\mathrm{Bu(Me_3Si)P{-}(P}t\mathrm{Bu)_2{-}P(SiMe_3)}t\mathrm{Bu}$ **240**

$t\mathrm{Bu(Me_3Si)P{-}[P(SiMe_3)]_2{-}P(SiMe_3)}t\mathrm{Bu}$ **241**

$t\mathrm{Bu_2P{-}[P(SiMe_3)]_2{-}P}t\mathrm{Bu_2}$ **242**

$\mathrm{(Me_3Si)_2P{-}[P(SiMe_3)]_2{-}P(SiMe_3)_2}$ **243**

In the preparation of **243** from $\mathrm{Li(Me_3Si)P{-}P(SiMe_3)_2}$ (**244**), which can be obtained by treating $\mathrm{H(Me_3Si)P{-}P(SiMe_3)_2}$ (**245**) with MeLi in toluene, two side products, $\mathrm{P_2(SiMe_3)_4}$ (**185**) and $\mathrm{[(Me_3Si)_2P]_2P(SiMe_3)}$ (**216**) were formed. These syntheses make use of the Li/Br replacement known from the formation of the fully silylated **185**, accessibly by treating $\mathrm{LiP(SiMe_3)_2}$ with 1,2-dibromoethane.[89]

Reactions between partly silylated *n*-tetraphosphanes and BuLi result in lithiated *n*-tetraphosphanides by Si−P bond cleavage: $\mathrm{Li}t\mathrm{BuP{-}[P(SiMe_3)]_2{-}P(SiMe)}t\mathrm{Bu}$ (**246**) (stable at −30 °C) from **241** and $t\mathrm{Bu_2P{-}PLi{-}P(SiMe_3){-}P}t\mathrm{Bu_2}$ (**247**) (yellow crystals) from **242**. The methanolysis of **247** yields the PH-substituted tetraphosphane $t\mathrm{Bu_2P{-}PH{-}P(SiMe_3){-}P}t\mathrm{Bu_2}$ **248** (needle-shaped crystals). In higher silylated derivatives P−P bond cleavage was observed in comparable reactions.[85]

4. Isotetraphosphanes

In this group the first representatives described are $\mathrm{P(PF_2)_3}$,[90] $\mathrm{P(PH_2)_3}$,[91] and $\mathrm{P(P}t\mathrm{BuBr)_3}$,[92] which was synthesized by treatment of $\mathrm{(P}t\mathrm{Bu)_3}$ with $\mathrm{PBr_3}$. Also $\mathrm{P(P}t\mathrm{BuH)_3}$[93] was accessible from $\mathrm{P(P}t\mathrm{BuBr)_3}$ and $\mathrm{LiAlH_4}$.

The alkali metal phosphanides $\mathrm{MP(SiMe_3)_2}$ (M = Li, Na, K) react with diorganochlorophosphanes to form isotetraphosphanes of the type $\mathrm{P(PR_2)_3}$ (R = Ph, cyclo-$\mathrm{C_6H_{11}}$, *i*Pr, *n*Pr, Et, Me) according to (100).

$$3\mathrm{MP(SiMe_3)_2} + 3\mathrm{R_2PCl} \xrightarrow[\substack{-2\mathrm{P(SiMe_3)_3} \\ -3\mathrm{MCl}}]{} \mathrm{P(PR_2)_3} \quad (100)$$

The reaction follows a stepwise pathway via intermediates such as $\mathrm{R_2P{-}P(SiMe_3)_2}$, $\mathrm{R_2P{-}P(SiMe_3)M}$, $\mathrm{(R_2P)_2P{-}SiMe_3}$, and $\mathrm{(R_2P)_2PM}$ to $\mathrm{P(PR_2)_3}$ by elimination of MCl and $\mathrm{P(SiMe_3)_3}$. Slow addition of the chlorophosphane to the alkali metal phosphanide at −40 °C is necessary to achieve this reaction; otherwise tetraorganodiphosphanes are obtained as main products. The corresponding reaction with $t\mathrm{Bu_2PCl}$ stops at the step of the triphosphane $\mathrm{(}t\mathrm{Bu_2P)_2PH}$ for sterical reasons.[94a,b]

The crystalline $\mathrm{P(P}t\mathrm{Bu_2)_3}$ was obtained by UV irradiation of the phospinophosphinidene $t\mathrm{Bu_2P{-}P{=}}$

Table 9. Syntheses of Silylated Isotetraphosphanes by Reaction of $LiP(SiMe_3)_{2-n}R_n$ ($n = 0, 1$; R = Ph, Me, *t*Bu) with Chlorinated Triphosphanes

	lithium phosphide	chlorinated triphosphane	isotetraphosphane	ref
	$LiP(SiMe_3)Ph$ (**250**)	$[Ph(Me_3Si)P]_2PCl$ (**251**)	$P[P(SiMe_3)Ph]_3$ (**256**)	98a
A	$LiP(SiMe_3)Me$ (**206**)	$[Me(Me_3Si)P]_2PCl$ (**252**)	$P[P(SiMe_3)Me]_3$ (**249**)	84, 95, 98a
	$LiP(SiMe_3)_2$ (**80**)	**252**	$[Me(Me_3Si)P]_2P{-}P(SiMe_3)_2$ (**257**)	98b
	$LiP(SiMe_3)t\mathrm{Bu}$ (**179**)	**252**	$[Me(Me_3Si)P]_2P{-}P(SiMe_3)t\mathrm{Bu}$ (**258**)	98a
B	**206**	$Me(Me_3Si)P{-}PCl{-}P(SiMe_3)_2$ (**253**)	**257** $Me(Me_3Si)P{-}PMe{-}P(SiMe_3)_2$ (**259**) (main product)	98a
	80	**253**	$Me(Me_3Si)P{-}P[P(SiMe_3)_2]_2$ (**260**) (less stability)	98a
	179	**253**	$Me(Me_3Si)P{-}P[P(SiMe_3)t\mathrm{Bu}]{-}P(SiMe_3)_2$ (**261**)	98a
	206	$Me(Me_3Si)P{-}PCl{-}P(SiMe_3)t\mathrm{Bu}$ (**254**)	**258**	98a
	80	**254**	**261**	98a
	179	**254**	$Me(Me_3Si)P{-}P[P(SiMe_3)t\mathrm{Bu}]_2$ (**262**)	98a
C	**206**	$[(Me_3Si)_2P]_2PCl$ (**211**)	*no isotetraphosphane* $P(SiMe_3)_3$ (**4**), $MeP(SiMe_3)_2$ (**41**) $[Me(Me_3Si)P]_2$ (**263**)	98a
	80	**211**	$\underset{\mathbf{212}}{P[P(SiMe_3)_2]_3} \rightarrow \underset{\mathbf{4}}{P(SiMe_3)_3} + P_4$	84, 98a
	179	**211**	*no isotetraphosphane* **4**, $t\mathrm{Bu}P(SiMe_3)_2$ (**217**)	98a
	206	$t\mathrm{Bu}(Me_3Si)P{-}PCl{-}P(SiMe_3)_2$ (**207**)	*no isotetraphosphane*, **4**, **217**, **41**	98a
	80	**207**	*no isotetraphosphane*, **4**, **217**	98a
	179	**207**	*no isotetraphosphane*, **4**, **217**	98a
	206	$[t\mathrm{Bu}(Me_3Si)P]_2PCl$ (**255**)	*no isotetraphosphane*, **217**, **41**, $[Me(Me_3Si)P]_2$ (**263**), cyclophosphanes	98a
	80	**255**	*no isotetraphosphane*, **4**, cyclophosphanes	98a
	179	**255**	$P[P(SiMe_3)t\mathrm{Bu}]_3$ (**264**), $t\mathrm{Bu}(Me_3Si)P{-}P(SiMe_3)t\mathrm{Bu}$ (**194**), $P_3(SiMe_3)t\mathrm{Bu}_2$ (**229**), $P_4[P(SiMe_3)t\mathrm{Bu}]_2t\mathrm{Bu}_2$ (**265**)	98a

$P(Me)t\mathrm{Bu}_2$. Whereas $P[P(SiMe_3)Me]_3$ (**249**) forms a flattened P_4 pyramid with $d(P{-}P) = 220.1$ pm,[95] the crystal structure analysis shows a planar geometry for $P(Pt\mathrm{Bu}_2)_3$ with a P−P bond distance of 219.1 pm.[96]

Tris(dialkylthiophosphinyl)phosphanes $P[P(S)R_2]_3$ were obtained in an analogous synthetic process with chlorides of thiophosphinic acid, as demonstrated in (101).

$$\underset{\mathbf{80}}{3LiP(SiMe_3)_2} + 3R_2P(S)Cl \xrightarrow[-2P(SiMe_3)_3 \atop -3LiCl]{} P[P(S)R_2]_3 \qquad (101)$$

$$R = Me, Et, n\mathrm{Pr}$$

Their formation proceeds stepwise as does the reaction with diorganochlorophosphanes in (100). Tetraalkyldiphosphanedisulfides were obtained by warming up the mixture. Investigations of $P[P(S)Me_2]_3$ showed that the compound with water forms H_3PO_3 and $HP(S)Me_2$, with HCl, PCl_3 and $HP(S)Me_2$, and with Br_2, PBr_3 and $BrP(S)Me_2$.[97]

Syntheses of silylated isotetraphosphanes use the typical reactions of functional phosphanes or silylphosphanes, respectively. In the last reaction step they are formed from the corresponding functional triphosphanes: (a) in reactions of triphosphanes, containing a Cl substituent at the secondary P atom with lithium phosphanides;[84,98a,b] (b) in reactions of P^2-lithiated triphosphanides with chlorophosphanes;[99a,b] (c) starting from a P halide via Si−P bond cleavage in a silylphosphane.[95]

The stability and reaction possibilities of silylated isotetraphosphanes are determined by their substituents ($SiMe_3$, *t*Bu, Me, Ph). Reactants and products are summarized in Tables 9 and 10.

In Table 9 the reactions of triphosphanes with the lithium phosphanides **206**, **80**, and **179** are divided into the groups A, B, and C.

(A) $[Me(Me_3Si)P]_2PCl$ (**252**) reacts with the lithium phosphanides to the corresponding isotetraphosphanes (102).

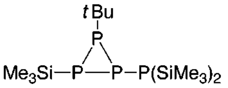
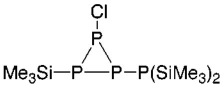
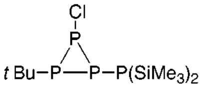
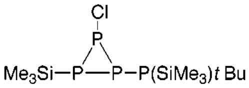
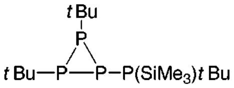
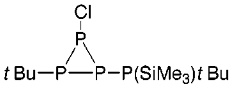
$$\underset{\mathbf{252}}{Me(Me_3Si)P{-}P(Cl){-}P(SiMe_3)Me} + LiP(SiMe_3)R'' \rightarrow Me(Me_3Si)P{-}P[P(SiMe_3)R'']{-}P(SiMe_3)Me + LiCl \qquad (102)$$

$$R'' = Me\ (\mathbf{249}) \quad R'' = SiMe_3\ (\mathbf{257}) \quad R'' = t\mathrm{Bu}\ (\mathbf{258})$$

(B) In the case of the somewhat sterically more loaded triphosphanes $Me(Me_3Si)P{-}PCl{-}P(SiMe_3)_2$ (**253**) and $Me(Me_3Si)P{-}PCl{-}P(SiMe_3)t\mathrm{Bu}$ (**254**), the corresponding isotetraphosphanes were still obtained; however, there occur already side reactions.

(C) With respect to the volume of their substituents *t*Bu and $SiMe_3$, the triphosphanes $[(Me_3Si)_2P]_2PCl$ (**211**), $t\mathrm{Bu}(Me_3Si)P{-}PCl{-}P(SiMe_3)_2$ (**207**), and $[t\mathrm{Bu}(Me_3Si)P]_2PCl$ (**255**) are quite similar. $[(Me_3Si)_2P]_2PCl$ (**211**) forms $P[P(SiMe_3)_2]_3$ (**212**) with **80** (−80 °C), as expected, but with $LiP(SiMe_3)Me$ (**206**) or **179**, the bond cleavage products **4** and **41** in addition to $[P(SiMe_3)Me]_2$ (**263**) and $t\mathrm{Bu}P(SiMe_3)_2$ (**217**), respectively, were obtained. Compound **255** reacts with **206** and **80** correspondingly. However, $P[P(SiMe_3)t\mathrm{Bu}]_3$ (**264**) is the main product in the reaction with **179**, accompanied by the diphosphane $t\mathrm{Bu}(Me_3Si)P{-}P(SiMe_3)t\mathrm{Bu}$ (**194**) and the cyclophosphanes $P_3(SiMe_3)t\mathrm{Bu}_2$ (**229**) and $P_4[P(SiMe_3)t\mathrm{Bu}]_2t\mathrm{Bu}_2$ (**265**).

Table 10. Syntheses of Silylated Isotetraphosphanes by Reactions of Lithiated Triphosphanides with Chlorophosphanes $R_{3-x}PCl_x$ (x = 1, 2, 3; R = tBu, Ph)

lithiated triphosphanide	chlorophosphane	isotetraphosphane	cyclophosphane	ref
$[(Me_3Si)_2P]_2PLi$ (**267**)	Ph_2PCl	$[(Me_3Si)_2P]_2P-PPh_2$ (**269**)		99b
267	tBu$_2$PCl	$[(Me_3Si)_2P]_2P-Pt$Bu$_2$ (**270**; white crystals)		99a
267	tBuPCl$_2$	$[(Me_3Si)_2P]_2P-P(Cl)t$Bu$_2$ (**271**)	 (**276**)	99b
267	PCl_3 (−78 °C)		 (**277**)	99b
tBu(Me$_3$Si)P−PLi−P(SiMe$_3$)$_2$ (**208**)	tBu$_2$PCl	tBu(Me$_3$Si)P−P(PtBu$_2$)−P(SiMe$_3$)$_2$ (**272**; colorless crystals; mp, 74 °C)		99a
208	PCl_3	"tBu(Me$_3$Si)P−P(PCl$_2$)−P(SiMe$_3$)$_2$"	 (**278**)	99a
[tBu(Me$_3$Si)P]$_2$PLi (**231**)	tBu$_2$PCl	[tBu(Me$_3$Si)P]$_2$P−PtBu$_2$ (**273**; colorless crystals; mp, 127 °C)	 (**279**)	99a
231	tBuPCl$_2$	[tBu(Me$_3$Si)P]$_2$P−PtBuCl (**274**; −78 °C)	 (**280**)	99a
231	PCl_3	"[tBu(Me$_3$Si)P]$_2$P−PCl$_2$" (not detectable)	 (**281**)	99a
tBu$_2$P−P(Li)−P(SiMe$_3$)$_2$ (**222**)	tBu$_2$PCl	(tBu$_2$P)$_2$P−P(SiMe$_3$)$_2$ (**275**; crystals; mp, 133 °C)	P$_4$[PtBu$_2$]$_2$(SiMe$_3$)$_2$ (**267**)	99a
(tBu$_2$P)$_2$PLi (**268**)	tBuPCl$_2$	(tBu$_2$P)$_2$P−P(Cl)tBu (−78 °C)	P$_4$[PtBu$_2$]$_2t$Bu$_2$ (**289**)	99a, 101
268	tBu$_2$PCl	(tBu$_2$P)$_3$P		99a

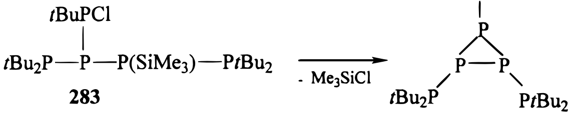
Depending on the silylation order of the triphosphane, on sterical requirements, and on the reactivity of the lithium phosphanide, three reactions determine the synthetic course competitively: (1) Cl substitution on the secondary P atom of the triphosphane; (2) transmetalation; (3) bond cleavage. With increasing silylation the thermal stability of the chlorinated triphosphane as well as of the formed isotetraphosphane decreases. Simultaneously, the tendency to P(SiMe$_3$)$_3$ elimination and P−P bond formation increases. Compared to the SiMe$_3$ group, the tBu group is the sterically more demanding substituent. The P−tBu bond is relatively inactive compared to the easily cleavable P−SiMe$_3$ bond. Within the lithium phosphanides, **206** is the more aggressive reagent followed by **179**. In the reactions with **80**, the thermal instability of the resulting isotetraphosphanes increases with the introduction of further SiMe$_3$ groups. The steric influence of Me and tBu groups, respectively, can be derived from the (thermally labile) Me(Me$_3$Si)P−P[P(SiMe$_3$)$_2$]$_2$ (**260**) still being isolable, whereas the tBu-substituted derivative tBu(Me$_3$Si)P−P[P(SiMe$_3$)$_2$]$_2$ (**266**) is not formed. In reactions with **206**, bond cleavage and transmetalation are favored, but the desired substitution reactions fall behind. In Table 10 such isotetraphosphanes are put together, which were prepared by reactions of lithiated triphosphanides with tBu$_2$PCl, tBuPCl$_2$, and PCl$_3$ and which carry tBu groups at different P atoms of the isotetraphosphane. The thermal stability increases with the amount of tBu substituents on the condition that the additional substituent does not cause a sterical overload. In reactions of this type, several side reactions known from the syntheses of PCl-substituted triphosphanes with lithium phosphanides (Table 9) can be omitted.

5. Silylated Isopentaphosphanes

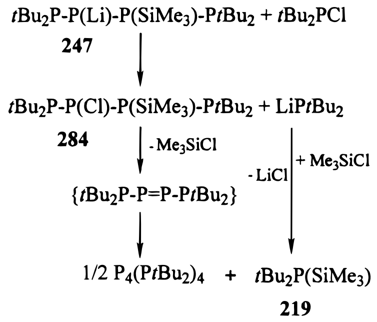
In the group of pentaphosphanes the basis compounds n-P$_5$H$_7$ and iso-P$_5$H$_7$ in detail were investigated with regard to their constitution and configuration.[100] Silylated isopentaphosphanes can be prepared from reactive n-tetraphosphanides in toluene at −40 °C, as demonstrated in (103), where two diastereomers in a 5:1 ratio were obtained.

$$\underset{\mathbf{247}}{t\mathrm{Bu_2P{-}PLi{-}P(SiMe_3){-}P}t\mathrm{Bu_2}} + t\mathrm{BuPCl_2} \xrightarrow[-\mathrm{LiCl}]{} \underset{\mathbf{283}}{t\mathrm{Bu_2P{-}P[P}t\mathrm{BuCl]{-}P(SiMe_3){-}P}t\mathrm{Bu_2}} \quad (103)$$

At 20 °C **283** eliminates Me$_3$SiCl and forms a P$_3$ cycle.

 (104)

The corresponding reaction of the lithium tetraphosphanide **247** with tBu$_2$PCl does not yield the isopentaphosphane, but the cyclotetraphosphane P$_4$(PtBu$_2$)$_4$ according to (105), analogously to the formation of P$_4$(PtBu$_2$)$_2t$Bu$_2$.[101]



(105)

Obviously sterical reasons prevent the formation of the tBu-substituted isopentaphosphane. A Li/Cl exchange proceeds, followed by the elimination of Me_3SiCl and the cyclization to $P_4(PtBu_2)_4$.

By treatment of the chlorinated triphosphanes $[tBu(Me_3Si)P]_2PCl$ (**255**) and $[(Me_3Si)_2P]_2PCl$ (**211**), respectively, with the lithiated diphosphane $LitBuP-P(SiMe_3)tBu$ (**203**), the isopentaphosphanes $[tBu(Me_3Si)P]_2P-PtBu-P(SiMe_3)tBu$ (**285**) and $[(Me_3Si)_2P]_2P-PtBu-P(SiMe_3)tBu$ (**286**) were accessible, proven by ^{31}P NMR investigations. Due to translithiations, side products resulted, from which the isopentaphosphanes could not be separated especially as they decompose during some days at room temperature.[102]

6. Hexaphosphanes $(R_2P)_2P-P(PR_2)_2$ (R = tBu, iPr)

Whereas the so far mentioned partly silylated tetraphosphanes, isotetraphosphanes and pentaphosphanes were formed in multistep reactions either of halogenated phosphanes with silylated lithium phosphanides or of PCl-substituted phosphanes with silylphosphanes, the hexaphosphanes $(tBu_2P)_2P-P(PtBu_2)_2$ and $(iPr_2P)_2P-P(PiPr_2)_2$ resulted from various attempts to prepare the phosphinophosphinidene−phosphoranes $(tBu_2P)_2P-P{=}P(Br)tBu_2$ and $(iPr_2P)_2P-P{=}P(Br)iPr_2$, respectively. Treating $LiP(PtBu_2)_2$ (**268**) at −70 °C with 1,2-dibromoethane generates the main product $tBu_2P-P{=}P(Br)tBu_2$ in addition to $(tBu_2P)_2PBr$, the latter reacting with an excess of **268** to form $(tBu_2P)_2P-P(PtBu_2)_2$.[103] $LiP(PiPr_2)_2$ reacts with 1,2-dibromoethane in THF to form the hexaphosphane $(iPr_2P)_2P-P(PiPr_2)_2$ as the main product in addition to the unstable $iPr_2P-P{=}P(Br)iPr_2$. Compared to the iPr group, which favors the formation of the hexaphosphane, the tBu group favors the formation of ylide. The P_6 skeleton of both molecules has a similar gauche conformation; however, the tBu groups cause the angles between the P atoms of the molecular axis and PR_2 groups to be about 10° larger than in the iPr case.[104]

VIII. Cyclophosphanes

Cyclophosphanes are accessible from linear silylphosphanes which contain both Cl and $SiMe_3$ substituents by means of Me_3SiCl elimination. 1,2-Substituted or 1,4-substituted silylphosphanes yield cyclotetraphosphanes, whereas cyclotriphosphanes result from 1,3-substituted starting molecules. Another group of cyclophosphanes, the $P_4(SiMe_2)_6$ adamantanes can be obtained by reacting Me_2SiCl_2 with a mixture of the phosphides $LiPH_2$, Li_2PH, and Li_3P via several cyclic intermediates. Also the thermal decomposition of linear and cyclic silylphosphanes yields stable products with an adamantane structure, but with sterically very demanding groups rather P−P and Si−P rings of small size are formed. Polycyclic silylphosphanes (with a pure P skeleton) result from the reactions of halogenosilanes with alkali metal phosphides M_3P_7.

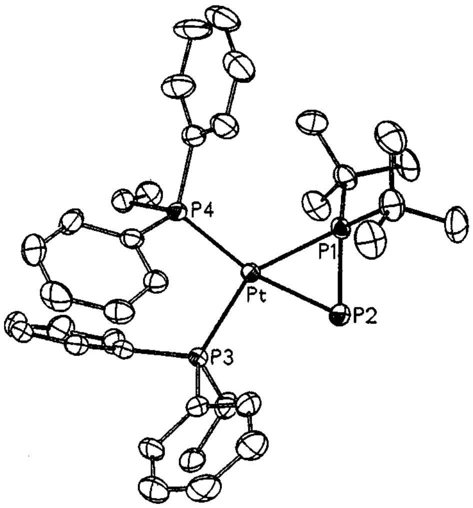
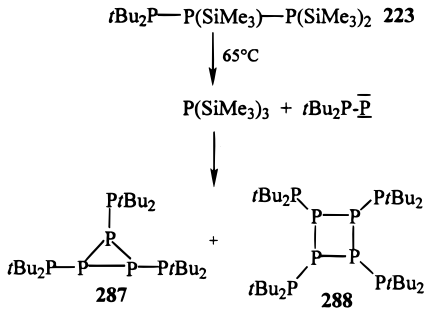


Figure 12. Molecular structure of $[\eta^2\text{-}\{tBu_2P-P\}Pt(PPh_2Et)_2]$. Reprinted with permission from 105b. Copyright 1997 Wiley-VCH Verlag GmbH.

A. Cyclophosphanes from Linear Silylated Tri-, Tetra-, and Pentaphosphanes

In the previous chapter already some linear tri-, tetra-, and pentaphosphanes with $SiMe_3$, tBu, Me, and Cl substituents were described, which are stable only at low temperature and form P rings with increasing temperature by elimination, in most cases, of Me_3SiCl.

By elimination of $P(SiMe_3)_3$, the triphosphane **223** yields the cyclophosphanes **287** and **288** via the intermediate tBu_2P-P according to (106).[105a]

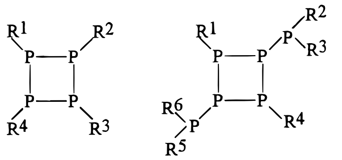


(106)

The tBu_2P-P moiety can be fixed as a complex ligand in the platinum compound $[\eta^2\text{-}\{tBu_2P-P\}Pt(PR_3)_2]$ (R_3 = Ph_3, Ph_2Et; Figure 12), which resulted from the reaction of $[\eta^2\text{-}\{H_2C{=}CH_2\}Pt(PR_3)_2]$ with the phosphinophosphinidene-phosphorane $tBu_2P-P{=}P(Me)tBu_2$ (**469a**).[105b]

1. Cyclotetraphosphanes

Silylated cyclotetraphosphanes with $SiMe_3$ and tBu groups result from partly silylated tetra-, isotetra-, and isopentaphosphanes, in which the functional



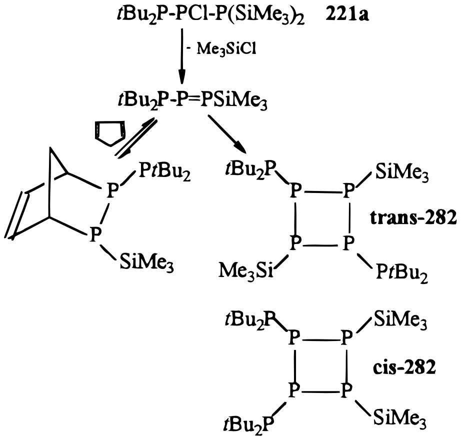
No.	R^1	R^2	R^3	R^4	R^5	R^6
220	*t*Bu	*t*Bu	$SiMe_3$	*t*Bu	-	-
238	$SiMe_3$	$SiMe_3$	$SiMe_3$	$SiMe_3$	-	-
239	$SiMe_3$	$SiMe_3$	*t*Bu	$SiMe_3$	-	-
219c	$SiMe_3$	*t*Bu	*t*Bu	$SiMe_3$	-	-
219t	$SiMe_3$	*t*Bu	$SiMe_3$	*t*Bu	-	-
289	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu
265	*t*Bu	*t*Bu	$SiMe_3$	*t*Bu	$SiMe_3$	*t*Bu
282	$SiMe_3$	*t*Bu	*t*Bu	$SiMe_3$	*t*Bu	*t*Bu

Figure 13. Cyclotetraphosphanes from silylated phosphanes.

$SiMe_3$ or Cl groups are situated either on the P^1 and P^4 atoms, or on directly neighboring P atoms in the chain. In the first case the four-membered ring results directly by Me_3SiCl elimination. In the second case the cyclotetraphosphane is formed via an intermediate stage with the $-P{=}P-$ group. The cyclotetraphosphanes, which were synthesized from silylated phosphanes, are summarized in Figure 13.

The cyclotetraphosphanes **219** and **220** were formed directly from partly silylated linear phosphanes by Me_3SiCl elimination. Compound **265**, *cis*- and *trans*-**282**, and **289** were obtained by dimerization of a P=P intermediate, which results from the elimination of Me_3SiCl from neighboring P atoms in the silylated triphosphane. Using the linear phosphanes $t\mathrm{Bu}_2P-P(SiMe_3)-Pt\mathrm{BuCl}$ (**290**) and **221a**, the presence of the intermediates $t\mathrm{Bu}_2P-P{=}Pt\mathrm{Bu}$ and $t\mathrm{Bu}_2P-P{=}P(SiMe_3)$ in the preparation of **265**, **282**, and **289**, respectively, was proven by trapping with cyclopentadienes (Scheme 18).[101]

Scheme 18



2. Reactions of Silylated Cyclotetraphosphanes and Silyl-Rich Linear Phosphanes

Whereas the *t*Bu-rich cyclophosphanes $P_4(t\mathrm{Bu})_3SiMe_3$ (**220**) and *trans*-$P_4(t\mathrm{Bu})_2(SiMe_3)_2$ (**219t**) with LiR (R = Me, *n*Bu) in THF form the cyclic phosphanides $LiP_4(t\mathrm{Bu})_3$ (**291**) and *trans*-$LiP_4(t\mathrm{Bu})_2SiMe_3$ (**292t**), respectively, the cyclophosphanes $P_4(SiMe_3)_4$ (**238**), $P_4(SiMe_3)_3t\mathrm{Bu}$ (**239**), and *cis*-$P_4(SiMe_3)_2(t\mathrm{Bu})_2$ (**219c**) react between −60 and −30 °C with ring opening. The reactivity decreases from **238** to **219c**. Cleavage of a P−P bond occurs in the first reaction step, and a lithiation with preservation of the skeleton was not observed. The following primary *n*-tetraphosphanides were detected: $Li(Me_3Si)P-P(SiMe_3)-P(SiMe_3)-P(SiMe_3)R$, R = Me (**293**), R′ = *n*Bu (**294**), from **238**; $Li(Me_3Si)P-Pt\mathrm{Bu}-P(SiMe_3)-P(SiMe_3)R$, R = Me (**295**), R′ = *n*Bu (**296**), from **239**; $Li(t\mathrm{Bu})P-Pt\mathrm{Bu}-P(SiMe_3)-P(SiMe_3)R$, R = Me (**297**), R′ = *n*Bu (**298**); $Li(Me_3Si)P-Pt\mathrm{Bu}-Pt\mathrm{Bu}-P(SiMe_3)R$, R = Me (**299**), R′ = *n*Bu (**300**), from **219c**. Under the described conditions they were formed only as reactive intermediates (except **299** and **300**). The fast isomerization to secondary *n*-tetraphosphanides with a 1,3-shift of Li and a $SiMe_3$ group was favored by the solvent THF: $(Me_3Si)_2P-P(SiMe_3)-P(Li)-P(SiMe_3)R$, R = Me (**293a**), R′ = *n*Bu (**294a**), from **238**; $(Me_3Si)_2P-Pt\mathrm{Bu}-P(Li)-P(SiMe_3)R$, R = Me (**295a**), R′ = *n*Bu (**296a**), from **239**; $(Me_3Si)t\mathrm{Bu}P-Pt\mathrm{Bu}-P(Li)-P(SiMe_3)R$, R = Me (**297a**), R′ = *n*Bu (**298a**), from **219c**. These processes were not observed in diethyl ether. The formation of the secondary phosphanides can be explained by the better donor ability of THF. Ether solutions of the *n*-tetraphosphanides, resulting from **238**, **239**, and **219c**, are stable only at low temperature. On warming to room temperature, rearrangements of the P skeleton take place, yielding P-rich compounds by elimination of $LiP(SiMe_3)_2$ (**80**), $P(SiMe_3)_3$ (**4**), $RP(SiMe_3)_2$, or $t\mathrm{Bu}P(SiMe_3)_2$ (**217**).[87]

This corresponds to the behavior of the silylated derivatives $(Me_3Si)_2P-P(SiMe_3)_2$ (**185**) and $[(Me_3Si)_2P]_2PSiMe_3$ (**216**), which are stable in pentane but react with BuLi in THF, yielding Li_3P_7, **4**, and **80**,[106] whereas **4** with BuLi forms the stable $LiP(SiMe_3)_2\cdot THF$.[51]

The course of these rearrangements is determined by the different number of the nonfunctional *t*Bu groups in the cyclotetraphosphanes. From **238**, Li_3P_7 resulted as the main product. The presence of *t*Bu groups prevents the formation of the P_7 skeleton. As such, the cyclopentaphosphanide $LiP_5t\mathrm{Bu}_4$, the cyclotriphosphanide $LiP_3t\mathrm{Bu}_2$, and the cyclotetraphosphane $P_4t\mathrm{Bu}_4$ were formed from **219c** already as end products.[87]

In an analogous way the cyclic lithium phosphanides $LiP_4t\mathrm{Bu}_3$, $LiP_5t\mathrm{Bu}_4$, and $LiP_3t\mathrm{Bu}_2$ were obtained by lithiation of $[t\mathrm{Bu}(Me_3Si)P]_2PH$ (**301**).[83]

The first reaction step in the formation of Li_3P_7 from silylated di- and triphosphanes is a lithiation: e.g. the diphosphane **185** forms $Li(Me_3Si)P-P(SiMe_3)_2$ (**244**). End products are Li_3P_7 and higher phosphides as well as **4** and **80**. The formation of **4** implies a desilylation of starting and intermediate compounds, respectively, and so results in the formation of P−P bonds. Compound **80** results from cleavage reactions. This stepwise process via P-richer and at the same time $SiMe_3$-poorer intermediates ends at Li_3P_7.[106] This corresponds to the lithiation of P_2H_4, yielding

Li_3P_7 with parallel PH_3 formation as described by Baudler et al.[107,108]

B. Cyclophosphanes from the Reaction of Chlorosilanes with Lithium Phosphanides

1. Reactions of Chlorosilanes with Li_3P, Li_2PH, and $LiPH_2$

By treating Li_3P (synthesized from PH_3 and BuLi) with Et_2SiCl_2, Parshall and Lindsey succeeded in the formation of the bicyclic compound $P(SiEt_2)_3P$ (**302**) in addition to the cyclic $(HP-SiEt_2)_2$ (**303**).[109] With the formation of $P(SiMe_2)_3P$ (**302a**) from Li_3P (also accessible from the elements[110]) and Me_2SiCl_2, this bicyclic type of compounds could be confirmed.[111]

$(PhP-SiPh_2)_3$ (**304**) and $(PhP-SiMe_2)_3$ (**305**) were synthesized by reacting $KHPPh/K_2PPh$ with Ph_2SiCl_2, or Li_2PPh with Me_2SiCl_2, respectively.[112] K_2PPh and $PhSiCl_3$ yield $(PPh)_6(SiPh)_4$ (**400**) with an adamantane structure.[113]

The reactions of Me_2SiCl_2 described in the following were realized with a lithium phosphanide mixture from PH_3/BuLi. The reaction products, the formation of which can be understood only by the participation of $LiPH_2$, Li_2PH, and Li_3P, are listed in Figure 14. Scheme 19 shows the reaction paths.

$H_2P-SiMe_2-PH-SiMe_2Cl$	**306**
$(H_2P-SiMe_2)_2PH$	**307**
$(HP-SiMe_2)_3$	**308**

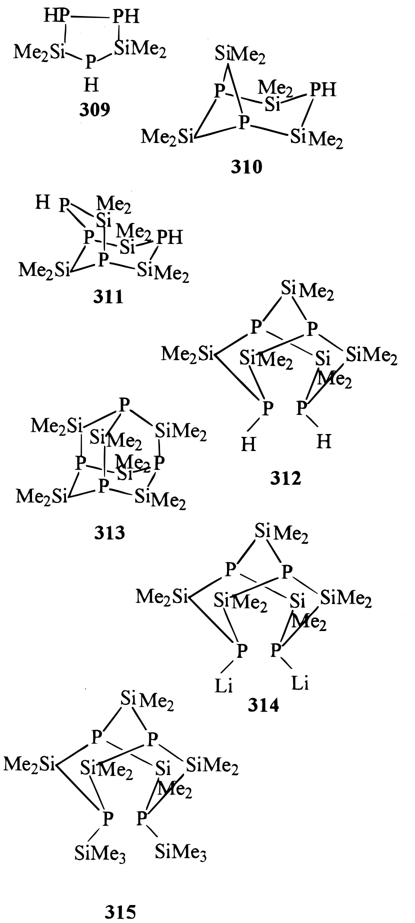
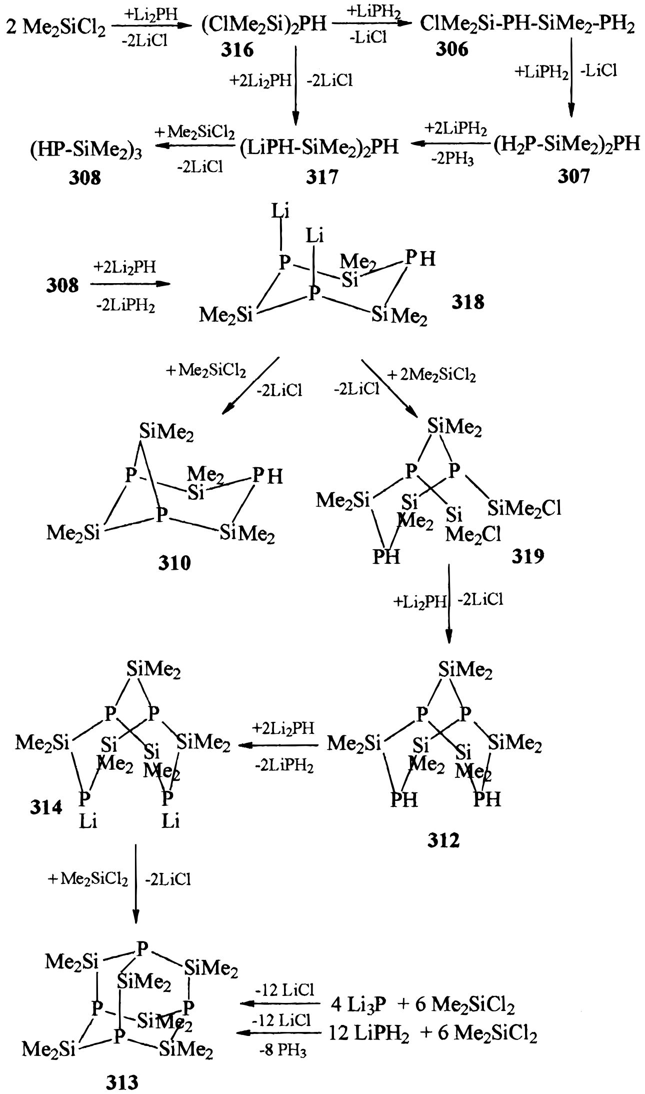


Figure 14. Products from the reaction of Me_2SiCl_2 with a lithium phosphanide mixture.

Scheme 19



The compounds **312** and **313** are the main products besides **308** and **310**. Reactions with an excess of lithium phosphanide imply a further metalation of PH groups and such favor the formation of polycyclic compounds. Also the lithiated derivative **314** was obtained, which can be transformed with Me_3SiCl to the silylated compound **315**.[65] Compound **312** (mp, 193 °C) furnished white crystals with the structure shown in Figure 15.

Molecule **312** has the symmetry mm (C_{2v}) and reacts as a bidentate chelate ligand, which with $(CO)_4Cr{\cdot}NBD$ forms compound $(SiMe_2)_5P_2(PH)_2Cr(CO)_4$ (**320**), showing an adamantane structure which contains a $Cr(CO)_4$ bridge (Figure 16).[114]

The ring skeleton of $(HP-SiMe_2)_3$ (**308**) forms several configurations, as shown by ^{31}P NMR investigations because the PH substituents occupy either the e,e,e/a,a,a or the a,e,e/e,a,a positions (Figure 17).[65]

The P atoms in the ring skeleton of $(PhP-SiPh_2)_3$ (**304**) are able to coordinate the $Mo(CO)_3$ group.[115]

In the cyclocondensation of $RSiHCl_2$ (R = Mes, Ph) with LiPH(Cy) (Cy = C_6H_{11}) the products $(CyP-SiHMes)_3$ (**321**) and $(CyP-SiHPh)_3$ (**322**) resulted, respectively. The sterically more demanding substituents preferably take an equatorial position in the

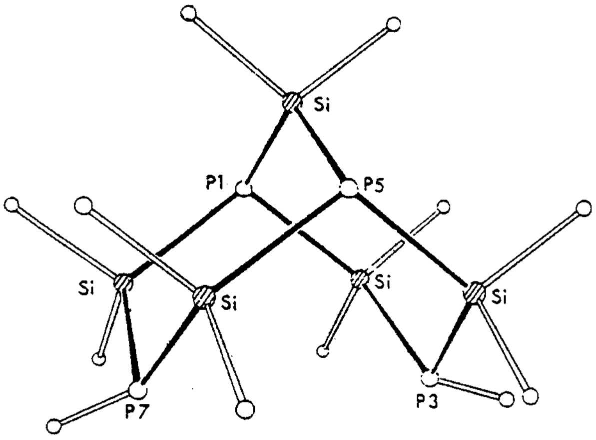


Figure 15. Molecular structure of 1,3,5,7-tetraphospha-2,4,6,8,9-pentasilabicyclo[3.3.1]nonane **312**. Reprinted with permission from ref 114. Copyright 1986 Wiley-VCH Verlag GmbH.

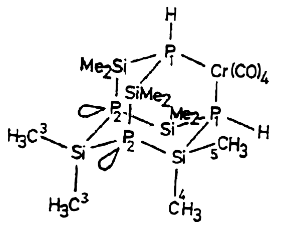


Figure 16. Adamantane structure of the transition metal complex $(SiMe_2)_5P_2(PH)_2Cr(CO)_4$ (**320**). Reprinted with permission from ref 114. Copyright 1986 Wiley-VCH Verlag GmbH.

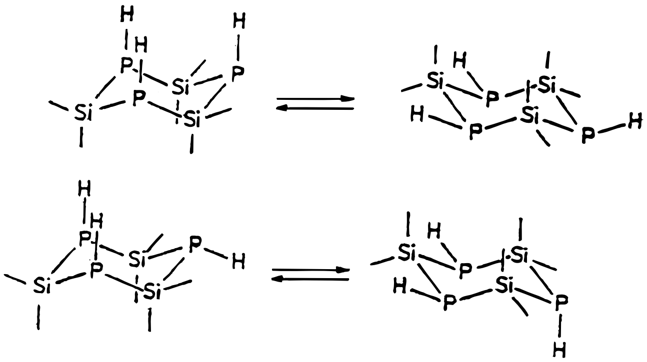
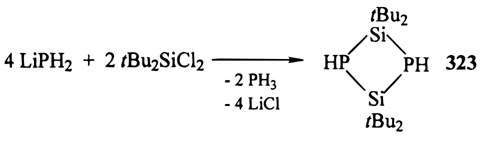


Figure 17. Configurations of the ring skeleton of $(HP-SiMe_2)_3$ (**308**). Reprinted with permission from ref 65. Copyright 1986 Wiley-VCH Verlag GmbH.

chair conformation of the P_3Si_3 six-membered rings, established by structural investigations.[116] However, $t\mathrm{Bu}_2SiCl_2$ reacts with $LiPH_2$ to the four-membered ring **323** (107), which is also accessible by treating Li_2PH with $t\mathrm{Bu}_2SiCl_2$.[114]



(107)

Under elimination of PH_3 **323** is monolithiated by $LiPH_2$ in DME to give the crystalline, isolable ring $HP(Si\,t\mathrm{Bu}_2)_2PLi\cdot 2DME$ (**323a**). The solvent-free $HP(Si\,t\mathrm{Bu}_2)_2PLi$ (**323b**) is accessible with *t*BuLi in toluene or pentane/hexane. The dimetalated $LiP(Si\,t\mathrm{Bu}_2)_2PLi$ (**323c**), even with an excess of *t*BuLi, can only be obtained in a mixture with **323b**. The reaction of **323b** with an excess of Me_2SiCl_2 at −70 °C in DME leads to a mixture of the compounds $HP(Si\,t\mathrm{Bu}_2)_2P-SiMe_2Cl$ (**324a**, 83%), $ClMe_2Si-P(Si\,t\mathrm{Bu}_2)_2P-SiMe_2Cl$ (**324c**, 28%), and $HP(Si\,t\mathrm{Bu}_2)_2PH$ (**323**, 7%), where a transmetalation between **324a** and **323b** caused the formation of **324b** (108). Compound **324c** forms colorless crystals.

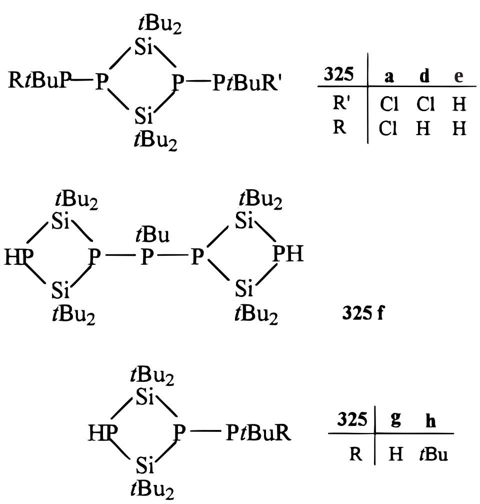
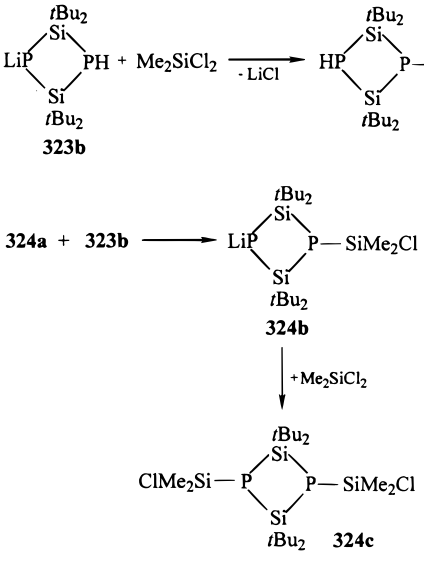
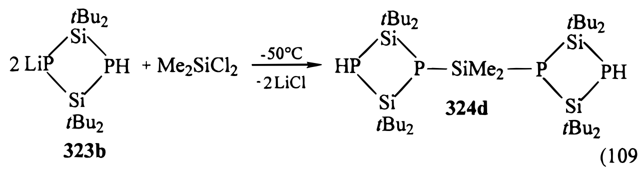


Figure 18. Products of the reaction of the $LiP(Si\,t\mathrm{Bu}_2)_2PH$ (**323b**)/$LiP(Si\,t\mathrm{Bu}_2)_2PLi$ (**323c**) mixture with $t\mathrm{BuPCl}_2$ in THF.



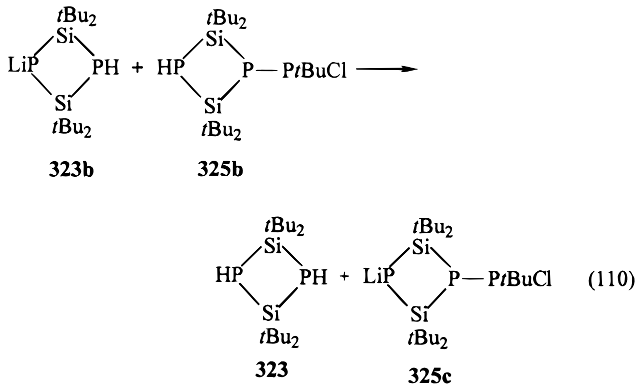
(108)

If the lithiation of **323** is performed at −70 °C and Me_2SiCl_2 is added to the reaction mixture at −50 °C, the snow-white glossy powder **324d** can be isolated (109).



(109)

$Me_3Si-P(Si\,t\mathrm{Bu}_2)_2P-SiMe_3$ (**324e**) and $HP(Si\,t\mathrm{Bu}_2)_2P-SiMe_3$ (**324f**) were prepared by reacting $HP(Si\,t\mathrm{Bu}_2)_2PH$ (**323**) with *t*BuLi in a molar ratio of 1:4 in pentane and subsequently adding of Me_3SiCl, via the intermediate $LiP(SitBu_2)_2PLi$ (**323c**). In the analogous reaction of a mixture of **323b** and **-c** with $tBuPCl_2$ in hexane, the main product $Cl(tBu)P-P(SitBu_2)_2P-P(tBu)Cl$ (**325a**) was formed in cis- and trans-configuration. The simultaneous formation of **323** can be explained by a transmetalation according to (110).



(110)

If the reaction was run in THF, the compounds shown in Figure 18 could be isolated with $HP(SitBu_2)_2P-P(tBu)-P(SitBu_2)_2PH$ (**325f**) as the main product.

The formation of the compounds **325d**, **325e**, and **325g** can be understood by a Li/Cl exchange, favored by the incomplete metalation of **323.** Remaining *t*BuLi attacks the terminal P(*t*Bu)Cl group forming the P(*t*Bu)Li unit and *t*BuCl, which react on to give the P(*t*Bu)H group, $Me_2C{=}CH_2$, and LiCl. The formation of **325h** results from the reaction of $HP(SitBu_2)_2P-PtBuCl$ (**325b**) with an excess of *t*BuLi.[117]

Reactions of LiPHMe with the chlorosilanes Me_2SiCl_2, $MeHSiCl_2$, and tBu_2SiCl_2, respectively, as well as those of LiPH*t*Bu with Me_2SiCl_2 demonstrate the sterical influence of the Me and *t*Bu groups on the reaction. Whereas with methylchlorosilanes the six-membered rings $(Me_2Si-PMe)_3$ (**326**) and $(MeHSi-PMe)_3$ (**327**) were obtained, LiPHMe reacts with tBu_2SiCl_2 to give the four-membered ring $(tBu_2Si-PMe)_2$ (**323d**). The cycles **326** and **327** resulted from compound $RR'Si(PHMe)_2$, which is expected to be formed initially by substitution of the chlorosilane, and then underwent cyclization by $MePH_2$ elimination according to (111).

$$3RR'Si(PHMe)_2 \rightarrow (RR'Si-PMe)_3 + 3MePH_2 \quad (111)$$
$$R = R' = Me\ (\mathbf{326})$$
$$R = Me,\ R' = H\ (\mathbf{327})$$

An even stronger sterical influence of the *t*Bu group can be observed in the reaction of Me_2SiCl_2 with LiPH*t*Bu, resulting in the compounds **328**, **329**, and **330** (Figure 19).

Compound $(Me_2Si)_3P_4tBu_2$ (**330**) forms colorless needles (mp, 154−156 °C), the crystal structure of which is shown in Figure 20.[118]

On heating to 190 °C, **328** forms **329** and **330** in addition to butane and 2-methylpropane and such demonstrates the steps of the formation path. Compound **328** can be lithiated using *n*BuLi (112) to give **331**, which reacts with the chlorosilanes Me_3SiCl, Ph_2SiCl_2, or $SiCl_4$, respectively, to give the compounds **332**−**334**, as shown in Scheme 20.

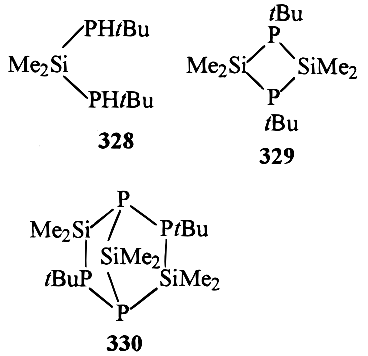


Figure 19. Products from the reaction of Me_2SiCl_2 with LiPH*t*Bu.

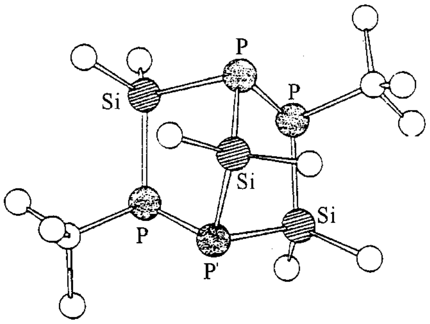
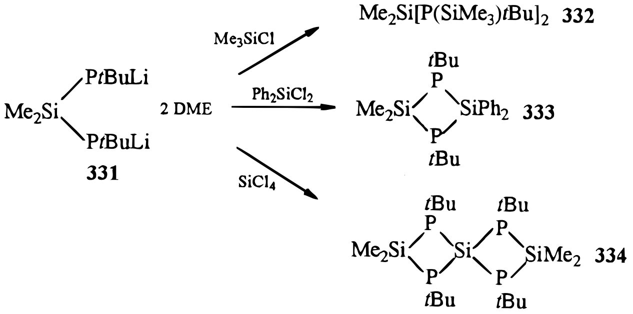


Figure 20. Molecular structure of $(Me_2Si)_3P_4tBu_2$ (**330**). Reprinted with permission from ref 118. Copyright 1978 Wiley-VCH Verlag GmbH.

Scheme 20



$$\underset{\mathbf{328}}{Me_2Si(PHtBu)_2} + 2nBuLi \rightarrow \underset{\mathbf{331}}{Me_2Si(PLitBu)_2} + 2C_4H_{10} \quad (112)$$

Boiling and melting points of the compounds **323d** and **326**−**334** are summarized in Table 11. The NMR data are listed in Table 12. All silylphosphanes are extremely sensitive to oxygen and moisture, but stable under inert gas. The lithiated derivatives are readily soluble in ether and aromatic hydrocarbons, but insoluble in saturatedhydrocarbons.[119]

2. Influence of the Substituents on the Ring Formation

The influence of sterically demanding groups on the reaction process is illustrated by the reaction of

Table 11. Melting and Boiling Points of 323d and 326−334

compd		mp[a] (°C)	bp (°C/Torr)
$(t\text{Bu}_2\text{Si}-\text{PMe})_2$	**323d**	167−169	−
$(\text{RR}'\text{Si}-\text{PMe})_3$			
R = R′ = Me	**326**	33−34	92−95/0.05
R = Me; R′ = H	**327**	42−43	122/0.3
$\text{Me}_2\text{Si}(\text{PR}t\text{Bu})_2$			
R = H	**328**	−	63−67/0.02
R = Li	**331**	88−92[b]	−
$\text{R} = \text{SiMe}_3$	**332**	35	104−108/0.01
$(\text{Me}_2\text{Si}-\text{P}t\text{Bu})_2$	**329**	−	114−118/0.05
$(\text{Ph}_2\text{Si}-\text{P}t\text{Bu})_2$	**333**	−	136/0.01
$(\text{Me}_2\text{Si})_3\text{P}_4t\text{Bu}_2$	**330**	154−156	−
$[\{\text{Me}_2\text{Si}(t\text{BuP})_2\}_2\text{Si}]$	**334**	133−135	−

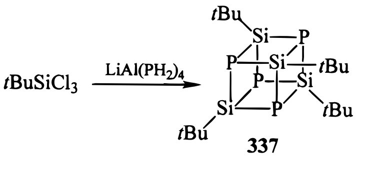
[a] Sealed tube. [b] With beginning decomposition.

Table 12. NMR Data of the Compounds 323d and 326−334

compd		$^3J_{\text{PSiCH}}$ (Hz)	$^2J_{\text{PCH}}$ (Hz)	$\delta(^{31}\text{P})$[a] (ppm)
$(t\text{Bu}_2\text{Si}-\text{PMe})_2$	**323d**	0.35	2.8[d]	+164.5
$(\text{RR}'\text{Si}-\text{PMe})_3$				
R = R′ = Me	**326**	5.1	2.4	+188.7
R = Me; R′ = H	**327**	4.0		+203.1[b,c] +187.1[b]
$\text{Me}_2\text{Si}(\text{PR}t\text{Bu})_2$				
R = H	**328**	4.05	12.2	+79.5 D
R = Li	**331**	1.8	11.2	+120.7
$\text{R} = \text{SiMe}_3$	**332**	2.4 4.0[d]	12.0[d]	+106.4
$(\text{Me}_2\text{Si}-\text{P}t\text{Bu})_2$	**329**	4.4	13.0	+78.9
$(\text{Ph}_2\text{Si}-\text{P}t\text{Bu})_2$	**333**	4.6	13.4	+83.7
$(\text{Me}_2\text{Si})_3\text{P}_4t\text{Bu}_2$	**330**	3.3; 0.45 4.5	13.7[d]	+172.0 +45.6
$[\{\text{Me}_2\text{Si}(t\text{BuP})_2\}_2\text{Si}]$	**334**	4.4	12.3	+61.3

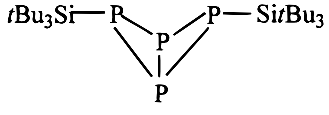
[a] Positive sign for high field shift to the standard. D = doublet. Singlets in the $^{31}\text{P}\{^1\text{H}\}$NMR spectra in addition to **327** and **330**. [b] Broad signals due to the $^{31}\text{P}-^{29}\text{Si}-^{31}\text{P}$ coupling ($^{31}\text{P}\{^1\text{H}\}$ NMR spectra). [c] Ratio of intensity is not determined exactly. [d] Pseudotriplet.

$\text{LiAl(PH}_2)_4$ with chlorosilanes RSiCl_3. If R = Me, Et, *i*Pr, or Ph, the silanes $\text{RSi(PH}_2)_3$ **27**−**30** were obtained (section III.B), but in the case of R = *t*Bu the compounds $t\text{BuSi(PH}_2)\text{Cl}_2$ (**335**) and $\text{H}_2\text{P}-(t\text{Bu})\text{Si}-(\text{Cl})-\text{P}[\text{Si}(t\text{Bu})\text{Cl}_2]_2$ (**336**) resulted, which changed into the silaphosphacubane $(\text{PSi}t\text{Bu})_4$ (**337**) (113), as proved by NMR investigations and X-ray analysis.[120]



337 (113)

Even more pronounced is the influence of the $t\text{Bu}_3\text{Si}$ group (supersilyl). The $t\text{Bu}_3\text{Si}$ radicals, accessible from $t\text{Bu}_3\text{Si}-\text{Si}t\text{Bu}_3$,[121] react with P_4, yielding $\text{P}_4(\text{Si}t\text{Bu}_3)_2$ (**338**) and $\text{P}_7(\text{Si}t\text{Bu}_3)_3$ (**339**) (Figure 21).[122]



338

Supersilylsodium $\text{NaSi}t\text{Bu}_3$ with P_4 in THF forms the disodium salt $(\text{Na})t\text{Bu}_3\text{SiP}-\text{P}{=}\text{P}-\text{PSi}t\text{Bu}_3(\text{Na})$ (**340**), which dimerizes to give the tetrasodium salt **341**.[123a]

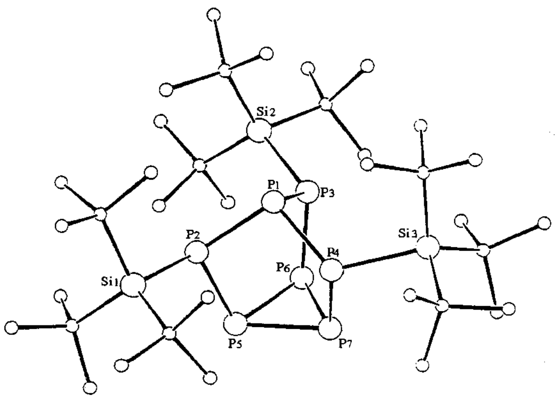
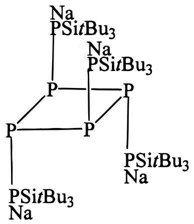
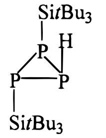


Figure 21. Molecular structure of $\text{P}_7(\text{Si}t\text{Bu}_3)_3$ (**339**). Reprinted with permission from ref 122. Copyright 1993 Wiley-VCH Verlag GmbH.

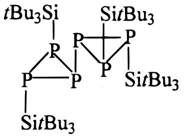


341

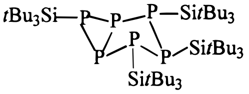
The THF adduct $\text{Na(THF)}_4\text{P}_3(\text{Si}t\text{Bu}_3)_2$ (**342a**) of the triphosphanide $\text{NaP}_3(\text{Si}t\text{Bu}_3)_2$ (**342**) was prepared by protolysis of **340** with an equimolar amount of CF_3COOH in THF. The protolysis of **342a** leads to the cyclotriphosphane **342b**, and its oxidation with $(\text{NC})_2\text{C}{=}\text{C(CN)}_2$ (TCNE) by dimerization of the P_3 skeleton to the isomeric hexaphosphanes **343a**,**b**.[123b]



342b



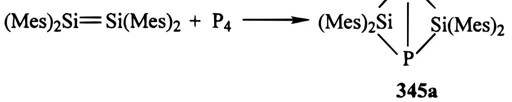
343a



343b

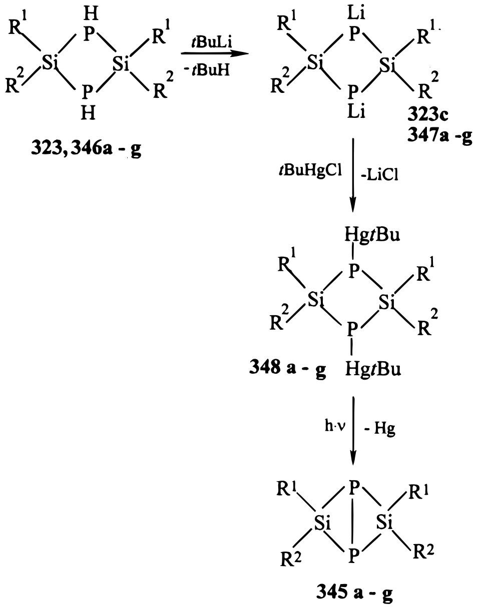
The pentaphosphanide $\text{Na}_2\text{P}_5(\text{Si}t\text{Bu}_3)_2$ (**344**) was obtained either by protolysis of $(t\text{Bu}_3\text{Si})_2\text{P}_4\text{Na(THF)}_n$ (**340**) with CF_3COOH in THF, by dissolving crystalline **340** in toluene ore by the reaction of P_4 with $t\text{Bu}_3\text{SiNa(THF)}_2$ in benzene. The orange THF adduct of the pentaphosphanide **344** has been established by X-ray structure analysis. Protolysis of **344** with the double molar amount of trifluoroacetic acid leads to the pale yellow three-membered pentaphosphane $\text{P}_3(\text{SiMe}_3)\{\text{P(H)Si}t\text{Bu}_3\}_2$ (**344a**) with a three-membered P_3-ring. A pentaphosphane $(t\text{Bu}_3\text{Si})_3\text{P}_5$ (**344b**) was also formed by oxidation with TCNE, whereas **344** was silylated with Me_2SiCl_2 to the bicyclic $\text{P}_5(\text{Si}t\text{Bu}_3)_3(\text{SiMe}_2)$ (**344c**).[124]

An important development in the chemistry of small Si−P rings was introduced with the reaction of tetramesityldisilene with P_4 (114).[125]



345a (114)

Such 1,3-diphospha-2,4-disilabicyclo[1.1.0]butanes are also accessible from the 1,3-diphospha-2,4-disilacyclobutanes, if the Si substituents R^1 and R^2 are sterically requiring groups (115).



(115)

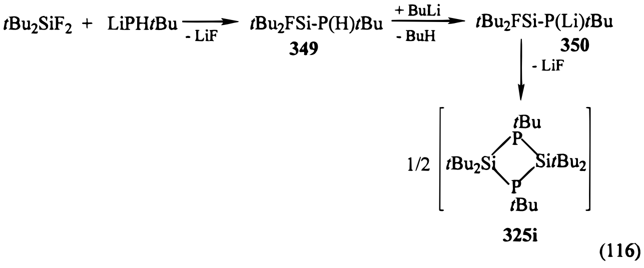
By photolysis the Hg cycles **348a**−**g** can be transformed into the Hg-free 1,3-diphospha-2,4-disilabicyclo[1.1.0]butanes **345a**−**g**.[126] Suitable substituents for syntheses of the P−Hg cycles **348a**−**g** are summarized in Table 13. All compounds have been characterized by ^{31}P and ^{29}Si NMR investigations. X-ray analyses of some characteristic samples were published.[127]

Table 13. Substituents R^1 and R^2 of $(R^1R^2Si{-}PH)_2$ (346a−g), $(R^1R^2Si{-}PLi)_2$ (347a−g), and the P−Hg cycles (348a−g)

	346, 347, 348							
	a	**b**	**c**	**d**	**e**	**f**	**g**	**323**
R^1	Mes	Mes	Mes	Mes	Mes	Is	Is	*t*Bu
R^2	Mes	*t*Bu	O*t*Bu	Xyl	CHEtMe	*t*Bu	Is	*t*Bu

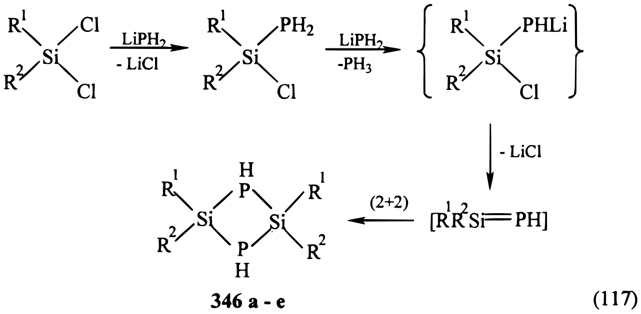
[a] Mes = 2,4,6-trimethylphenyl; Xyl = 2,6-dimethylphenyl; Is = 2,4,6-triisopropylphenyl

All of the up to now described 1,3-diphospha-2,4-disilacyclobutanes $[R^1P{-}Si(R^2)_2]_2$ with [R^1 = H, R^2 = *t*Bu;[6,65] R^1 = H, R^2 = *i*Pr;[128] R^1 = *t*Bu, R^2 = NMe(SiMe$_3$)[129]] and also those according to (116) accessible compound $(tBu_2Si{-}PtBu)_2$ (**325i**)[129] may not be transferred from the cycles of type **346** to the bicycles **345** as demonstrated in (115).



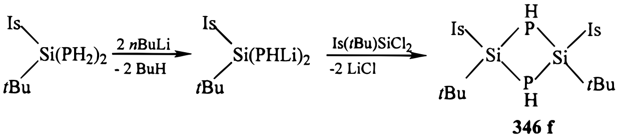
(116)

Mechanism 117 describes the formation of the P_2Si_2 cyclobutanes **346a**−**e** starting from bulky substituted dichlorodiorganosilanes $R^1R^2SiCl_2$. The so far not detected intermediate $R^1R^2Si(Cl)PHLi$ should lead to the cyclobutanes **346a**−**e** via the phosphasilenes and their spontaneous head-to-tail dimerization.[127]



(117)

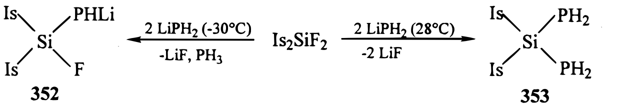
Compound **346f** can be only obtained in a different synthetical way (118).



(118)

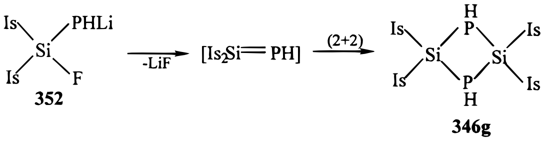
The reaction process as shown in (117) has been proved by investigations of Klingebiel et al.[128,129] They synthesized the isolable $[(Me_3Si)MeN]_2(F)Si{-}P(H)$-*t*Bu (**351**) by treating $[(Me_3Si)MeN]_2SiF_2$ with LiP(H)*t*Bu, which after cyclization with *t*BuLi gives $[\{(Me_3Si)MeN\}_2Si{-}PH]_2$ (**346i**).

In an analogous way the reaction of Is_2SiF_2 (Is = 2,4,6-triisopropylphenyl) with $LiPH_2$ at −30 °C in THF leads to $Is_2(F)Si{-}PHLi$ (**352**), whereas at 28 °C the disubstituted silane **353** is obtained (119). Under N_2 atmosphere **352** is stable at 28 °C in THF.



(119)

Elimination of LiF from **352** in hexane affords the P_2Si_2 cyclobutane **346g**, probably via the phosphasilene (120).



(120)

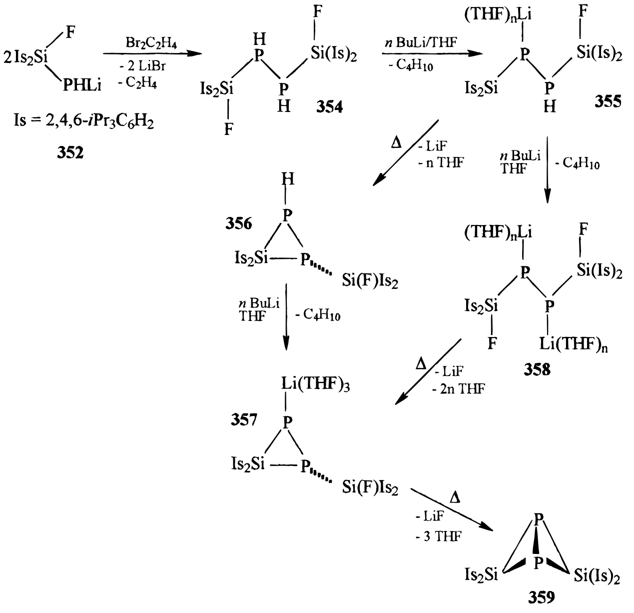
Compound **352** is characterized by ^{29}Si, ^{19}F, and ^{31}P NMR investigations as well as by hydrolysis to $Is_2(F)SiPH_2$ as by reaction with Me_3SiCl, yielding $Is_2(F)Si{-}PH(SiMe_3)$. For some of these compounds X-ray crystal structure determinations were run.

The Si_2P_2 cyclobutanes with sterically requiring groups (**346c**−**e**) form colorless crystals and were isolated as mixtures of diastereomers. However, crystals of **346a,b**,**f,g** were obtained exclusively as trans isomers.[130a]

Starting from the bulky substituted bis(fluorosilyl)phosphane *t*Bu(R)FSi−PH−SiF(R)*t*Bu (R = 2,4,6-iPr$_3$C$_6$H$_2$) and its lithiation with *n*BuLi in THF, the corresponding lithium phosphanide can be synthesized. In this molecule the Li center is 4-fold-coordinated by two THF molecules, the phosphorus atom, and the fluorine atom. Heating a solution of this phosphanide to 70 °C results in loss of LiF and formation of the 2-phospha-1,3-disilaallyl fluoride *t*Bu(R)FSi−P=Si(R)*t*Bu with a Si=P bond length of 2.053(2) Å, in which no intramolecular or intermolecular Si−F−Si contacts are observable, proved by crystal structure analysis. A fluctuation of the fluorine atom (1,3-sigmatropic shift) is observed at about 40 °C.[130b]

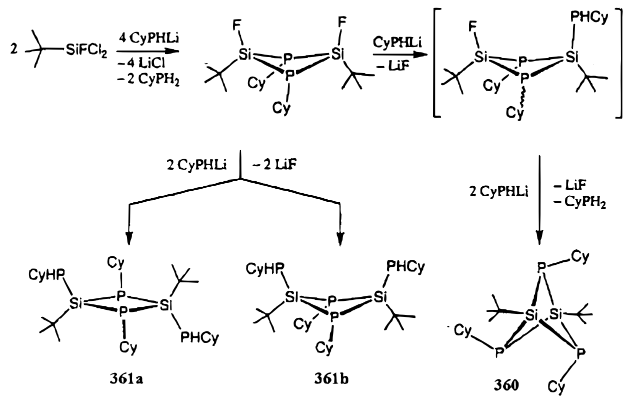
Is$_2$(F)Si−PH−PH−Si(F)Is$_2$ (**354**) (synthesized from Is$_2$(F)Si−PHLi (**352**) and 1,2-dibromoethane) reacts with *n*BuLi, yielding the phosphanide **355**, which is converted by thermolysis and LiF elimination into the corresponding diphosphasilacyclopropane **356**. Lithiation of the P−H function in **356** leads to the derivative **357**, which furnishes on heating the butterfly-like 1,3-diphospha-2,4-disila-bicyclo[1.1.0]butane **359** (Scheme 21). The diphosphasilacyclopropanes **356** and **357** have been characterized by single crystal X-ray analysis.[130c]

Scheme 21



Treating *t*BuSiFCl$_2$ with LiPH(Cy) (Cy = cyclohexyl) in a molar ratio of 1:3 in THF generates the propellane-like bicyclosilaphosphane (*t*BuSi)$_2$(PC$_6$H$_{11}$)$_3$ (**360**). The synthesis succeeds only in THF, and not with other silanes such as *t*BuSiCl$_3$. The reaction starts with a LiCl elimination and a cyclocondensation followed by a SiF/P(H)Cy group replacement. Another LiF elimination from the formed intermediate leads to the bicyclosilaphosphane (*t*BuSi)$_2$(PC$_6$H$_{11}$)$_3$ (**360**). Scheme 22 shows the formation of the additionally produced diastereometric cycles **361a** and **361b**. Compounds **360**, **361a**, and **361b** have been investigated by NMR spectroscopy and also by X-ray analysis (Figures 22 and 23). The bonding relations as well as the unusual ring geometry in **360** were dealt with.[130d]

Scheme 22[a]



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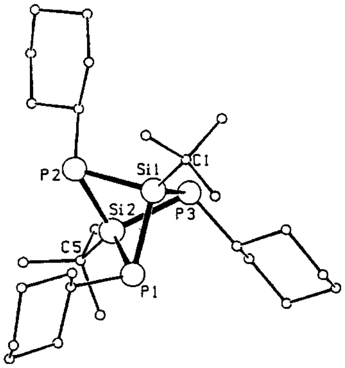


Figure 22. Molecular structure of the bicyclosilaphosphane (*t*BuSi)$_2$(PC$_6$H$_{11}$)$_3$ (**360**). Reprinted with permission from ref 130d. Copyright 1994 Wiley-VCH Verlag GmbH.

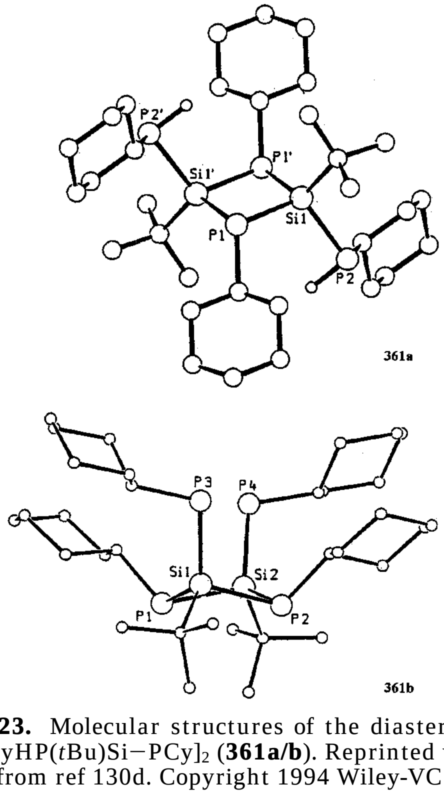
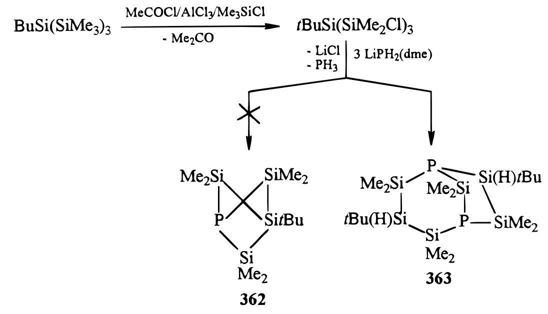


Figure 23. Molecular structures of the diastereometric cycles [CyHP(*t*Bu)Si−PCy]$_2$ (**361a/b**). Reprinted with permission from ref 130d. Copyright 1994 Wiley-VCH Verlag GmbH.

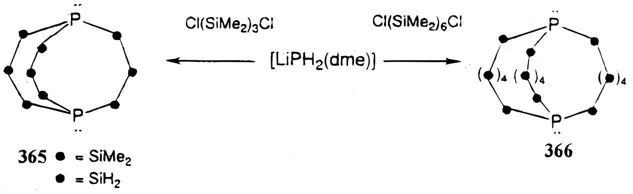
Scheme 23



In an attempt to synthesize the bicyclic molecule **362** with high ring strain, tBuSi(SiMe$_2$Cl)$_3$ was reacted with LiPH$_2$(DME) (Scheme 23). However, this leads to a complex mixture, from which only the bicyclic cyclosilaphosphane **363** could be isolated in 29% yield and characterized by ^{1}H, ^{31}P, and ^{29}Si NMR and a single crystal X-ray analysis, respectively.[130e]

The skeleton of **363** is a constitutional isomer of the bicyclic P(SiMe$_2$−SiMe$_2$)$_3$P (**364**), which results from the cyclocondensation of Cl(SiMe$_2$)$_2$Cl with LiPH$_2$(DME). This synthetic strategy can be applied to expanded polysilane systems. Thus, the reaction of LiPH$_2$(DME) with the dichlorooligosilanes Cl(SiMe$_2$)$_3$Cl and Cl(SiMe$_2$)$_6$Cl leads to the bicycles **365** and **366**, respectively (Scheme 24).[130f]

Scheme 24[a]



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C. Polycyclic Silylphosphanes

In this section polycyclic silylated phosphanes as well as polycycles with Si−P groups in the molecular skeleton are described. Their formation is generally based on the reaction of white phosphorus with Na/K alloy and the subsequent addition of chlorosilanes.

1. Compounds with a P$_n$Si$_3$ Molecular Skeleton (n = 4, 7, 11)

The above-mentioned synthesis leads to the isolation of the heptaphosphanortricyclane P$_7$(SiMe$_3$)$_3$ (**367**).[131] The structure of this molecule is ascertained by ^{31}P NMR studies as well as by X-ray structure determination (Figure 24).[132]

The metalation of **367** with tBuLi or **80** yields Li$_3$P$_7$, but the reactions are not fully understood.[106] The formation of Li$_3$P$_7$ by lithiation of P$_2$H$_4$ with nBuLi or LiPH$_2$ and the bonding type (fluctuating bonds) were investigated by Baudler et al.[107] Another way to obtain the higher lithium phosphanides Li$_3$P$_7$, Li$_2$P$_7$R, and LiP$_7$R$_2$ turned out to be the reaction of white phosphorus with lithium alkyls LiR (R = Me, tBu). Addition of Me$_3$SiCl affords the silyl-substituted products P$_7$(SiMe$_3$)$_3$ (**367**), P$_7$(SiMe$_3$)$_2$R (R = Me (**368**), tBu (**370**)), and P$_7$(SiMe$_3$)R$_2$ (R = Me (**369**), tBu (**371**)). With higher amounts of tBuLi, the cycles LiP$_4t$Bu$_3$ and LiP$_3t$Bu$_2$ are formed, which can be silylated to P$_4$(SiMe$_3$)tBu$_3$ (**220**) and P$_3$(SiMe$_3$)tBu$_2$ (**229**) by Me$_3$SiCl.[133]

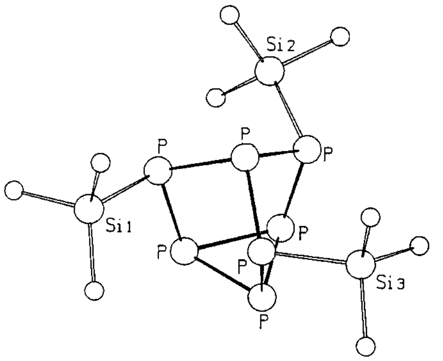


Figure 24. Molecular structure of P$_7$(SiMe$_3$)$_3$ (**367**).

P$_7$(SiMe$_3$)$_3$ (**367**) can be lithiated with Li$_3$P$_7$ (molar ratio 2:1) to LiP$_7$(SiMe$_3$)$_2$ (**372**) and to Li$_2$P$_7$SiMe$_3$ (**373**) (1:2).[134] The metalation with Li$_3$P$_7$·3DME produces mixtures of LiP$_7$(SiMe$_3$)$_2$ (**372**), Li$_2$P$_7$(SiMe$_3$) (**373**), and Li$_3$P$_7$ from which pure **372** can be extracted with toluene as an isomeric mixture (s, as). Similarly, the isomers of LiP$_7$R$_2$ (R = Et, iPr, iBu) can be extracted from the mixtures obtained by reacting Li$_3$P$_7$ with alkylbromides. In solution at about 20 °C the s-isomers of LiP$_7$R$_2$ form slowly the as-isomers, whereas the latter up to 70 °C do not show any inversion.[135] LiP$_7$R$_2$ as well as Li$_2$P$_7$R (R = SiMe$_3$ (**373**), Me, tBu) show the typical valence tautomerism[134] as previously described by Baudler et al. for Li$_2$P$_7$H.[136]

The homologues P$_7$(SiR$_3$)$_3$ (R$_3$ = Ph$_3$ (**374**), H$_3$ (**375**), H$_2$Me (**376**), Me$_2$PEt$_2$ (**377**)) can be synthesized by reacting Li$_3$P$_7$·3DME with the suitable halogenosilanes.[137,138] The methanolysis of P$_7$(SiMe$_3$)$_3$ (**346**) leads to H$_3$P$_7$.[139]

The disilane tBu$_3$Si−SitBu$_3$ with bulky substituents[140] reacts with white phosphorus to form P$_7$(SitBu$_3$)$_3$ (**339**). The compound is identified by NMR investigations and a single crystal structure determination (Figure 21).[122]

Structural investigations on various compounds R$_3$P$_7$ indicate no radical changes on the bridge P atoms (P^e) of the P$_7$ skeleton by the substituents iBu, nBu, and Et$_2$P−SiMe$_2$. The steric demands of the (tBu)$_3$Si groups cause an increase of the exocyclic bond angles at the equatorial P atoms as well as a longer P−Si distance. A far-reaching modification of the P$_7$ skeleton can be achieved by complexation.[141]

It is assumed that the formation of P$_7$(SiMe$_3$)$_3$ (**367**) by reaction of P$_4$ and Na/K with Me$_3$SiCl proceeds via the intermediates Na$_3$P$_7$ or K$_3$P$_7$, respectively.[131]

Pure M$_3$P$_{11}$ (M = Na, Cs)[142] with Me$_3$SiCl gives the silyl-substituted undecaphosphane P$_{11}$(SiMe$_3$)$_3$ (**378**). The isolated light yellow crystals are not stable. X-ray

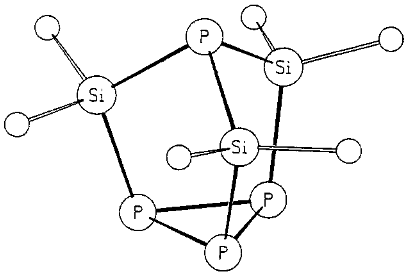
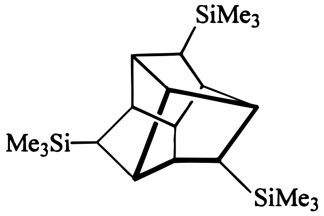


Figure 25. Molecular structure of $P_4(SiMe_2)_3$ (**379**).

investigations show that the molecule consists of six linked five-membered phosphorus rings.[143]

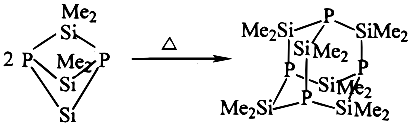


378

Treating a white phosphorus/Na/K reaction mixture with Me_2SiCl_2 gives the hexamethyltrisilatetraphosphanortricyclane $P_4(SiMe_2)_3$ (**379**), in which $SiMe_2$ groups occupy the positions of the equatorial $PSiMe_3$ units in **367**.[144] Figure 25 shows the molecular structure of **379**.[132]

2. Silylphosphanes with Adamantane Structure

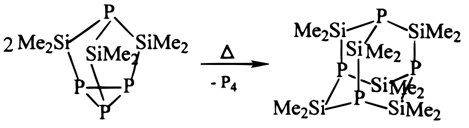
Adamantanes with alternating Si and P atoms in the molecular skeleton are preferably formed compounds, as their formation from linear and cyclic silylphosphanes suggests. So the bicyclic $P(SiMe_2)_3P$ (**380**) dimerized above 120 °C to the more stable adamantane cage of **313** (121).[111]



380 **313** (121)

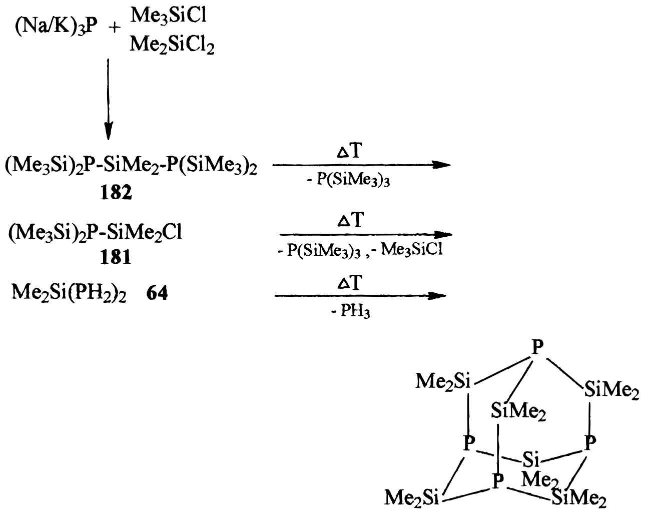
Further syntheses for the adamantane **313** use the thermolysis of various Si-methylated silylphosphanes as sources for the P–$SiMe_2$ and $SiMe_2$ units in the construction of the adamantane skeleton (Scheme 25). The reaction of **64** corresponds to the preparation of $(Me_2Ge)_6P_4$ from $Me_2Ge(PH_2)_2$.[145]

Even compound **379** can be transformed into the adamantane **313** in a sealed tube at 230–240 °C (60 h) (122). Compound **313** is stable at least up to 400 °C.[146] Its structure was derived from a single crystal structure determination.[147]



379 **313** (122)

Scheme 25



313

Table 14. Compounds Formed in the Thermolysis of $(Me_3Si)_2P–SiEt_2Cl$ (381)

adamantane		amount (%)	liquid products
$P_4(SiMe_2)_6$	**313**	20	$P(SiMe_3)_3$ (**4**)
$P_4(SiMe_2)_5(SiEt_2)$	**385**	40	$P(SiMe_3)_2[SiEt_2(Me)]$ (**391**)
$P_4(SiMe_2)_4(SiEt_2)_2$	**386a,b**	20	$P(SiMe_3)[SiEt_2(Me)]_2$ (**392**)
$P_4(SiMe_2)_3(SiEt_2)_3$	**387a–c**	5	Me_3SiCl
$P_4(SiMe_2)_2(SiEt_2)_4$	**388a,b**		$Et_2MeSiCl$
$P_4(SiMe_2)(SiEt_2)_5$	**389**		(**4**:**391**:**392** = 5:4:1)
$P_4(SiEt_2)_6$	**390**	<1	

The thermolysis of $(Me_3Si)_2P–SiMe_2Cl$ (**181**) and its derivatives $(Me_3Si)_2P–SiEt_2Cl$ (**381**), $(Me_3Si)_2P–SiMeEtCl$ (**382**), and $(Et_3Si)_2P–SiEt_2Cl$ (**383**) (300 °C, 14d, sealed tube) results exclusively in Si–P adamantanes. If however $(Me_3Si)_2P–SiPh_2Cl$ (**384**) is employed (just two Me groups of **181** are replaced by two Ph groups), only trisilylphosphanes substituted by Me and Ph groups are formed.

In Table 14, the products from **381** are summarized. The geometry of the adamantane skeleton determines the number of isomers of the formed adamantanes $P_4(SiMe_2)_{6-x}(SiEt_2)_x$ ($x = 0–6$): for **386** and **388** two isomers and for **387** three isomers. Their isolation and concentration was achieved by fractionated crystallization, and their characterization, by ^{31}P NMR investigation and mass spectrometry.

In the analogous thermolysis of **382**, **313**, and $P_4(SiMe_2)_5(SiMeEt)$ (**392**) are the main products in addition to further adamantanes $P_4(SiMe_2)_{6-x}(SiMeEt)_x$ ($x < 6$). The latent chirality of the EtMeSi group gives rise to a considerably greater number of isomers if $x = 2–6$. According to (123), the thermolysis of $(Et_3Si)_2P–SiEt_2Cl$ (**383**) generates $P_4(SiEt_2)_6$ (**390**) already at 80 °C.

$$\underset{\mathbf{383}}{6(Et_3Si)_2P{-}SiEt_2Cl} \rightarrow \underset{\mathbf{390}}{P_4(SiEt_2)_6} + \underset{\mathbf{394}}{2P(SiEt_3)_3} + 6Et_3SiCl \quad (123)$$

As complex as the course of these syntheses may be, it is always the formation of the favored adamantane

Table 15. Silaphosphaadamantanes from the Reactions of Dichlorosilanes with P_4 and Na/K

dichlorosilane	silaphosphaadamantanes	
$EtMeSiCl_2$	$P_4(SiMeEt)_6$	**395**
Et_2SiCl_2	$P_4(SiEt_2)_6$	**390**
$PhMeSiCl_2$	$P_4(SiMePh)_6$	**396**
$(vinyl)(Me)SiCl_2$	$P_4[Si(Me)(vinyl)]_6$	**397**
$MeHSiCl_2$	$P_4(SiHMe)_6$	**398**
$Et_2SiCl_2/MeHSiCl_2$	$P_4(SiHMe)(SiEt_2)_5$	**399**

skeleton which dominates the reaction. $P(SiR_3)_3$ and R_3SiCl are side products from cyclization reactions, and no poorly soluble products are produced. The detection of $P_4(SiMe_2)_4(SiEt_2)_2$ (**386**) in the thermolysis of **381** points out that even a Si−C cleavage must occur as a precondition for the formation of the $SiMe_2$ bridges.[148] Another way into the chemistry of the silaphosphaadamantanes $P_4(SiR_2)_6$ employs the reaction of P_4 with Na/K alloy and dichlorosilanes R_2SiCl_2 (Table 15). The process is determined by the ratio of P_4 to Na/K as well as by the nature of the substituent R as becomes obvious by the formation of the already mentioned **379**[144] and **380**.[111] $P_4(SiMeEt)_6$ (**395**) resulted if a ratio of 1:3 for P_4 to Na/K in DME was used (124).

$$3(Na/K) + {}^1/_4P_4 + {}^3/_2EtMeSiCl_2 \rightarrow \underset{\mathbf{395}}{{}^1/_4P_4(SiMeEt)_6} + 3MCl\ (M = Na, K) \quad (124)$$

Compound **395** forms colorless crystals and consists of a mixture of eight chiral isomers (four diastereomeric pairs of enantiomers) due to the presence of the EtMeSi groups in the adamantane skeleton. This synthesis of **395** turned out to be much more effective than the thermolysis of **382**[148] with yields less than 1% of **395**.

The functional Si groups in the skeleton of the adamantanes **397**−**399** give rise to further substitutions.

The reaction of the alkali metal phosphide with Ph_2SiCl_2 does not lead to the corresponding adamantane, whereas the replacement of a phenyl by a methyl group yields the adamantane $P_4(SiMePh)_6$ (**396**). tBu_2SiCl_2 does not react with P_4 and Na/K.[149]

The formation of $(PhP)_6(SiPh)_4$ (**400**) with an inverse adamantane structure in which the SiPh units serve as bridgeheads and the PPh groups as binding links is described by Schumann and Benda in the reaction of $PhSiCl_3$ with K_2PPh.[113]

IX. Transition Metal Complexes of Linear and Cyclic Silylphosphanes

Numerous metal complexes incorporating metal carbonyls and silylated monophosphanes have been described, whereas not many information exist about the complex chemistry of metal carbonyls with partly silylated di- and triphosphane ligands. The molecular structures of cyclic, silicon functional silylphosphanes can be fixed by complex formation. In the trisilatetraphosphanortricyclene, the complexation starts at the basal P atoms allowing the linkage over the complex ligand.

Organosubstituted phosphanes PR_3 (R = Me, Et, Ph) as Lewis base are able to displace ligands out of the coordination sphere of the metal to form stable carbonylphosphane complexes. Thereby, the reaction speed and the stability of the yielded compounds are influenced by the nucleophilic properties of the PR_3 molecule provided an unchanging carbonyl.

The first transition metal complexes incorporating silylphosphane ligands such as $P(SiMe_3)_3$ **4** or $R_nP(SiMe_3)_{3-n}$ were reported by Schumann and Stelzer.[150a−c]

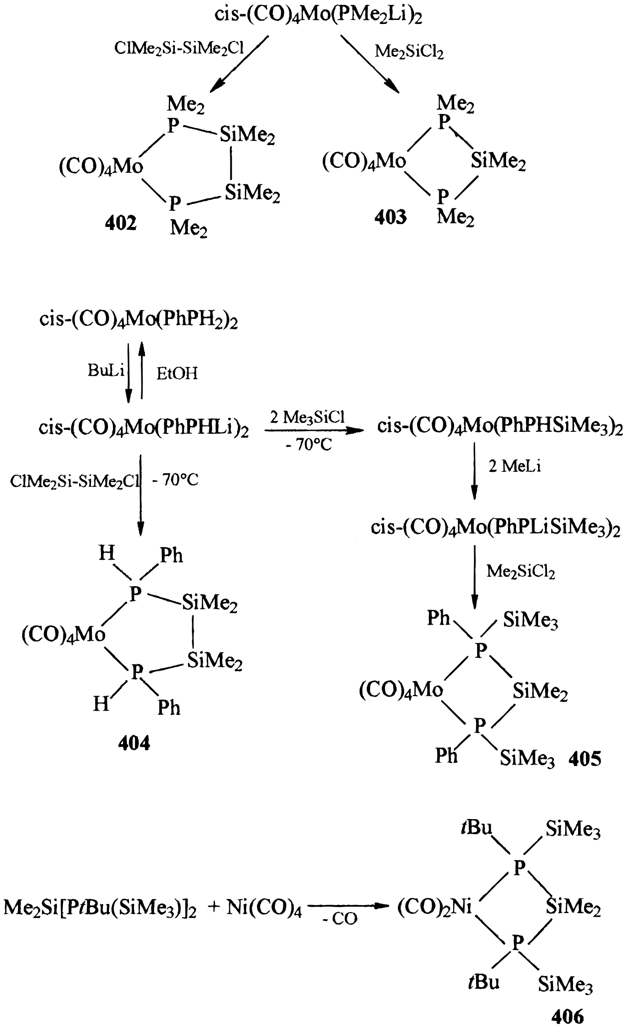
Complex compounds of the type $R(Me_3Si)_2PM(CO)_x$ and $(Me_3Si)_3PM(CO)_x$ could be synthesized in the reaction of the corresponding silylphosphanes and metal carbonyls $M(CO)_{x+1}$ under UV irridiation with displacement of one CO ligand (125).[150b−f]

$$(Me_3Si)_nPR_{3-n} + M(CO)_{x+1} \xrightarrow[-CO]{} (CO)_xM{\cdot}PR_{3-n}(SiMe_3)_n \quad (125)$$

M	x	R	n
Cr	5	Ph	1,2,3
		tBu	0,1,2
Mo	5	Ph	1,2,3
		tBu	0,1,2
W	5	Ph	1,2,3
		tBu	0,1,2
Ni	3	tBu	0,1,2,3
Fe	4	tBu	0,1,2,3

The cobalt complexes $[Co_2(CO)_6\{P(SiMe_3)_3\}_2]$ (**401**) and $[Co_2(CO)_6\{PtBu_2(SiMe_3)\}_2]$ (**401a**) were synthesized by reacting $Co_2(CO)_8$ with **4** and $PtBu_2(SiMe_3)$ (**558**), respectively, with elimination of two CO ligands.[150g] Thus, the silylphosphanes $(Me_3Si)_nPR_{3-n}$ in contrast to their SiH and SiF analogous $P(SiH_3)_3$ (**5**),[151a] $H_3Si{-}PH_2$ (**1**),[151b] and $F_3Si{-}PH_2$ (**54**)[47] show basic properties, which can be attributed to the influence of the substituents on the Si−P bond. The ability of silylated di- and triphosphanes with the substituents Bu, $SiMe_3$, Me, Ph, and H to form complexes was investigated in reactions with $Cr(CO)_5(THF)$. Unfortunately no single crystals from the obtained products could be isolated. Its characterization based on data of mass spectra and ^{31}P NMR. The position of the Cr ligands were deduced by comparing the chemical shifts ($\delta^{31}P$) of the used di- and triphosphanes, respectively, with them of the formed chromium carbonyl complexes. ($\Delta(^{31}P)$ = differences in chemical shifts). Hence the formulation of complex compounds with P−P−Cr rings results.[152a] Single crystal X-ray investigations on the finally accessible crystalline compounds $Li(THF)_2Et_2O[Cr(CO)_4\{\eta^2{:}\eta^1\text{-}(tBu_2P)_2P\}Cr(CO)_5]$, $[Cr(CO)_5\{\eta^1\text{-}(tBu_2P)_2PH]$, and $[Cr(CO)_4\{\eta^2\text{-}(tBu_2P)_2PH]$ from the reaction of $Li(THF)_2[\eta^2\text{-}(tBu_2P)_2P]$ with $Cr(CO)_5(THF)$ and $Cr(CO)_4NBD$, respectively, allowed the comparison of these results with those of the formerly obtained spectroscopical data. They are in agreement for the first two chromium complexes and the phosphanide $Li(THF)_2[\eta^2\text{-}(tBu_2P)_2P]$, but not for $[Cr(CO)_4\{\eta^2\text{-}(tBu_2P)_2PH]$. Based on the chemical shifts, a structure with a P−P−Cr ring was assumed for this complex.[152b] Therefore not all structural formulas deduced from the ^{31}P NMR data are reliable, and a

Scheme 26

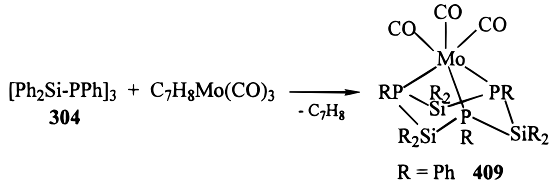


further clarification by means of single crystal X-ray analysis is necessary.[186]

In the ring compounds **402**−**406** (Scheme 26) the silylphosphanes serve as chelating ligands in transition metal complexes.[153,154] The nickel complex **406** forms two isomers in a ratio of 1:1.[155]

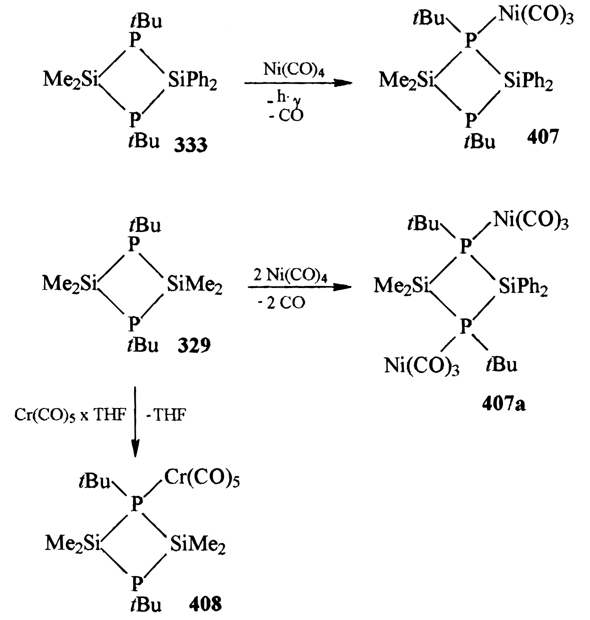
Monocyclic silylphosphanes as [$Me_2Si-P\textit{t}Bu-SiPh_2-P\textit{t}Bu$] (**333**) and [$Me_2Si-P\textit{t}Bu]_2$ (**329**) react with $Ni(CO)_4$, depending on the molar ratio to the nickel complex **407** or to the dinuclear complex **407a**, respectively (Scheme 27). Both compounds are decomposed either by light or when stored in vacuo. Compound **329** yields with $Cr(CO)_5$(THF) the chromium complex **408**; however, the analogous dinuclear chromium complex is not accessible. Compound **408** is more stable than the nickel complex **407**.[155]

In the triphosphatrisilacyclohexane **304** the ring skeleton allows the coordination of a $Mo(CO)_3$ group to the three P atoms of the six-membered ring according to (126).[115]

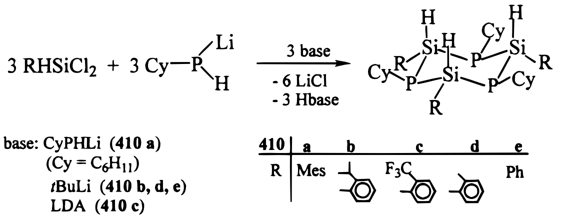


(126)

Scheme 27



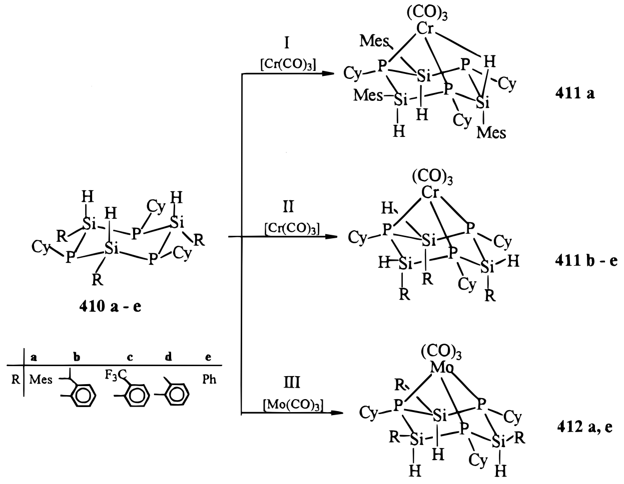
Furthermore, various derivatives of 1,3,5-triphospha-2,4,6-trisilacyclohexanes were synthesized (127) to study the sterical influence of the Si substituents.



(127)

By complexation with $M(CO)_3$ moieties (M = Cr, Mo) three different types of products were obtained (Scheme 28), the structures of which were determined by the different sterical requirements of the aryl substituents as well as by the size of the metal. These types can be characterized by (1) formation of a Cr−H−Si three-center, two-electron bond (**411a**), (2) axial aryl substituent at Si (**411b**−**e**), and (3) equatorial substituent at Si (**412a,e**).

Scheme 28



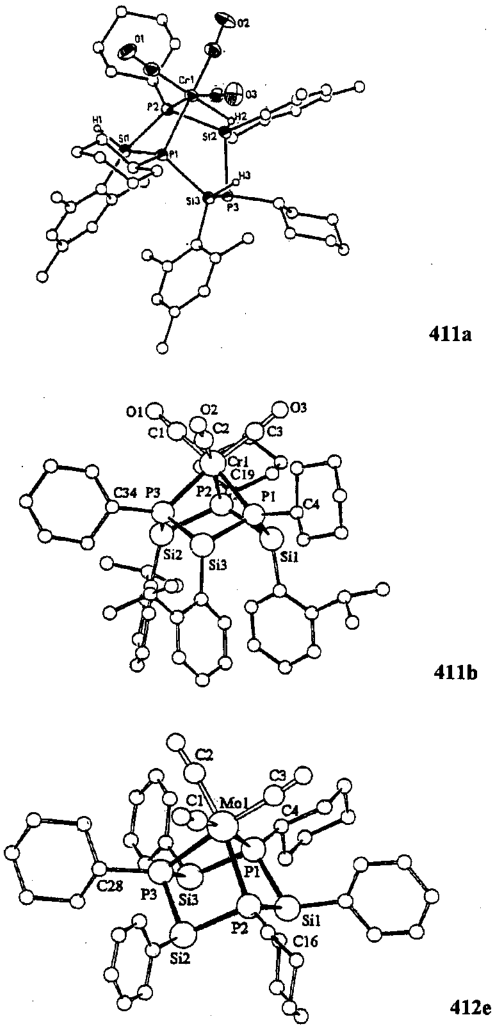
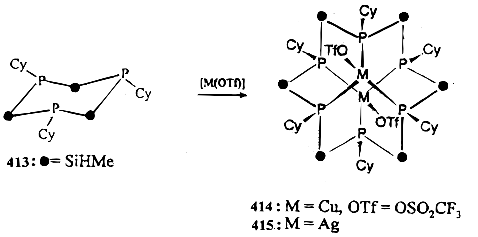


Figure 26. Molecular structures of the compounds **411a**, **411b**, and **412e**. Reprinted with permission from refs 156 and 157. Copyright 1992, 1996 Wiley-VCH Verlag GmbH.

Scheme 29[a]



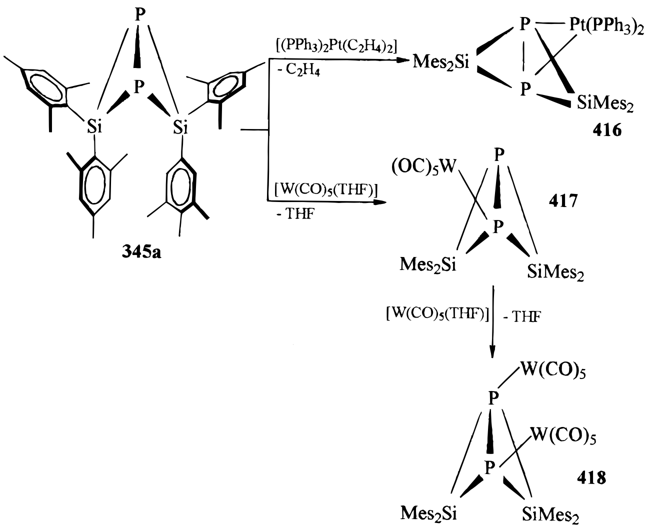
[a] Reprinted with permission from ref 158. Copyright 1997 Wiley-VCH Verlag GmbH.

The molecular structures of the complexes **411a**, **411b**, and **412e** are shown in Figure 26.[156,157]

Using the strong Lewis acids [M(OTf))] (M = Cu, Ag; OTf = OSO_2CF_3) in the reaction with (CyP–$SiHMe)_3$ (**413**), the complexes **414** and **415** with the cyclic twelve-membered ligand $[(CyP)_6(SiMeH)_6)]$ were synthesized (Scheme 29). Both compounds could be identified by single-crystal structure determinations.[158]

The complexation of the P_2Si_2 bicyclobutane **345a**, produced from white phosphorus and $Mes_2Si{=}SiMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$), with $W(CO)_5{\cdot}THF$ or $[(Ph_3P)_2$-$Pt(C_2H_4)]$, respectively, leads to the complexes **416**–**418** (Scheme 30). All compounds are characterized by ^1H and ^{31}P NMR investigations, **418** additionally by a X-ray structure determination. (Figure 27).[125]

Scheme 30



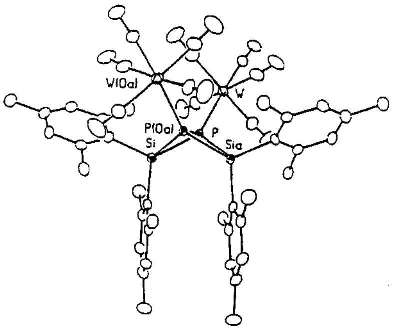
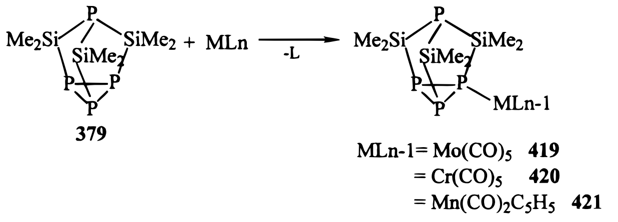


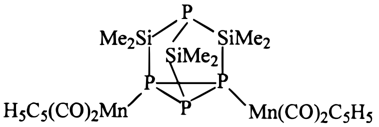
Figure 27. Molecular structure of the complex **418**. Reprinted with permission from ref 125. Copyright 1989 Wiley-VCH Verlag GmbH.

By UV irradiation the hexamethyltrisilatetraphosphanortricyclane $P_4(SiMe_2)_3$ (**379**) generates crystalline complexes with $Mo(CO)_6$, $Cr(CO)_5{\cdot}THF$, or Mn(η-C_5H_5)$(CO)_2{\cdot}THF$, respectively, in which $P_4(SiMe_2)_3$ serves as a monodentate ligand. One phosphorus atom of the cyclotriphosphane is coordinated to the metal atom (128).



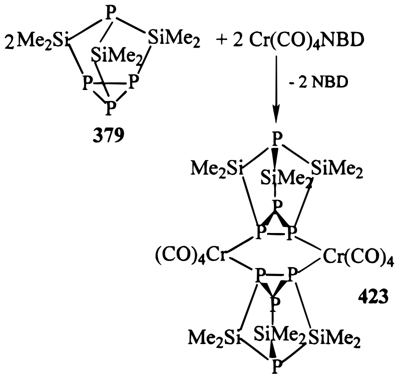
(128)

Using an excess of Mn(η-C_5H_5)$(CO)_2{\cdot}THF$, a mixture of **421** and of the dinuclear manganese complex **422** was obtained.[159]



422

The reaction of **379** with tetracarbonyl−norbornadiene−chromium(0) in a molar ratio of 1:1 leads to the dimeric $(CO)_4Cr[\eta\text{-}(Me_2Si)_3P_4]_2Cr(CO)_4$ (**423**) (129). In contrast to (128), no mononuclear complex was observed.



(129)

In none of the above mentioned reactions the top phosphorus atom of **379** was found to be the coordinating atom. The products were identified by NMR investigations, mass spectra as well as elemental analysis.[159] Additional single crystal X-ray analyses of the chromium complexes $P_4(SiMe_2)_3Cr(CO)_5$ (**420**) and $[P_4(SiMe_2)_3Cr(CO)_4]_2$ (**423**) demonstrated that only minor changes in the bond distances were caused by the chromium fragment.[160]

An even higher coordination of the Cr moiety by **379** can be achieved with chromium complexes which contain a triply coordinated ligand (130).

$$\begin{aligned}&\underset{\mathbf{379}}{3P_4(SiMe_2)_3} + 2RCr(CO)_3 \rightarrow\\ &\qquad R = C_6H_6\\ &\qquad R = C_7H_8\\ &\qquad \underset{\mathbf{424}}{[P_4(SiMe_2)_3]_3[Cr(CO)_3]_2} + 2R \quad (130)\end{aligned}$$

Another possible synthesis for **424** is by heating $P_4(SiMe_2)_3Cr(CO)_5$ (**420**) in benzene or THF (120 °C, sealed tube) for several hours. According to an X-ray investigation, complex **424** has the structure shown in Figure 28 and can be characterized as an octahetero[2.2.2]barrelane, the 3-fold axis of which goes through the both chromium atoms.[161]

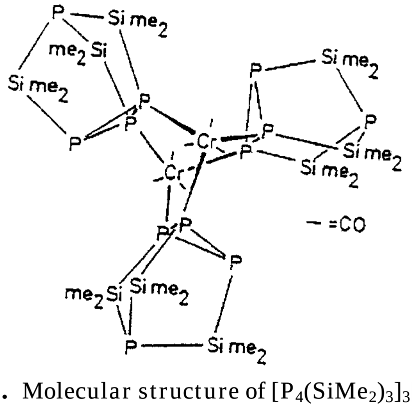


Figure 28. Molecular structure of $[P_4(SiMe_2)_3]_3[Cr(CO)_3]_2$ (**424**). Reprinted with permission from ref 161. Copyright 1982 Wiley-VCH Verlag GmbH.

$P_7(SiMe_3)_3$ (**367**) reacts with $Cr(CO)_5\cdot THF$, furnishing various chromium carbonyl complexes in which the $Cr(CO)_5$ fragment is bonded to an equatorial phosphorus atom (P^e) and only with increasing coordination also to a basal P atom (P^b).[162]

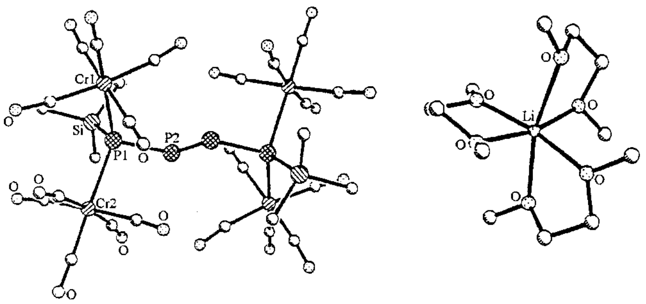


Figure 29. Structure of the dianion and of the solvated cation of the compound $[Li(DME)_3]_2\{(SiMe_3)[Cr(CO)_5]_2P{-}P{=}P{-}P[Cr(CO)_5]_2(SiMe_3)\}$ (**425**). Reprinted with permission from ref 164. Copyright 1992 Wiley-VCH Verlag GmbH.

A comprehensive report about the reactions of heptaphosphanes P_7R_3 (R = Et, *i*Pr, $SiMe_3$) with transition metal complexes was given by Baudler and Glinka.[163]

With regard to its formation and structure, the ionic $[Li(DME)_3]_2\{(SiMe_3)[Cr(CO)_5]_2P{-}P{=}P{-}P[Cr(CO)_5]_2(SiMe_3)\}$ (**425**) is completely different from the previously described complexes. The compound, obtained from $LiP(SiMe_3)_2[Cr(CO)_5]$ (**426**) with 1,2-dibromoethane, forms a salt composed of a dianion $R_2R'_4P_4^{2-}$ ($R = SiMe_3$, $R' = Cr(CO)_5$) and solvated Li^+ cations (Figure 29).[164]

X. Silylated Phosphorus Ylides

Phosphorus ylides due to their special bonding conditions and reactivity form a unique class of compounds. Their synthetic applicability can be widely extended by incorporating silyl and, even better, Si-functional substituents into the P ylides. Phosphorus ylides with a pure P skeleton, the phosphinophosphinidene-phosphoranes, make still another area of ylide chemistry accessible.

A. Formation of C-Silylated Phosphorus Ylides

The development of silylated phosphorus ylides goes back to the 1960s and is based on the synthesis of $Me_3P{=}CH{-}SiMe_3$ (**427**) by two different procedures as demonstrated in (131) and (132).[165]

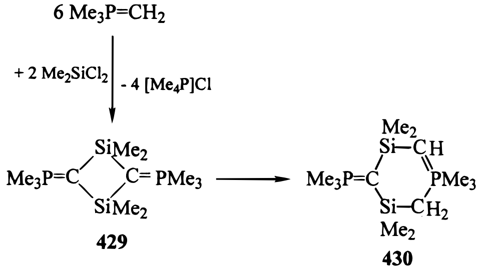
$$[Me_3P{-}CH_2{-}SiMe_3]Cl + Ph_3P{=}CH_2 \rightleftharpoons \underset{\mathbf{427}}{Me_3P{=}CH{-}SiMe_3} + [Ph_3P{-}CH_3]Cl \quad (131)$$

$$[Me_3P{-}CH_2{-}SiMe_3]Cl + n\text{BuLi} \xrightarrow[-C_4H_{10}\ -LiCl]{} \underset{\mathbf{427}}{Me_3P{=}CH{-}SiMe_3} \quad (132)$$

The range of applications could be extended by the introduction of Si-functional substituents by “trans-silylation” (133).[166,167]

$$\underset{\mathbf{428}}{Me_3P{=}C(SiMe_3)_2} + 2Me_2SiCl_2 \rightarrow \underset{\mathbf{428a}}{Me_3P{=}C(SiMe_2Cl)_2} + 2Me_3SiCl \quad (133)$$

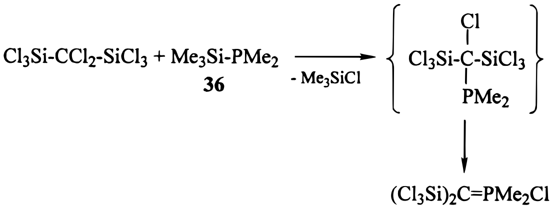
The cyclic silylalkylidenephosphorane **429** was obtained as demonstrated in (134),[168] but undergoes slowly an isomerization yielding the less strained six-membered ring **430**.[169]



(134)

Mathiason and Miller[170] and Schmidbaur and Tronich[171] reported the phosphanylation to $(Me_3Si)(PMe_2)C{=}PMe_3$ (**431**) by reacting **427** with Me_2PCl, and Karsch[172] described the reaction of **428** with Me_2PCl yielding $(Me_2P)_2C{=}PMe_3$ (**432**). Furthermore, the reactions of $Ph_3P{=}C(SiMe_3)_2$ (**433**) with PX_3 (X = Cl, Br),[173] the ylidylphosphanes ($Ph_3P{=}CR{-}PR_2$) and -diphosphanes ($Ph_3P{=}CR{-}PR{-}PR_2$)[174] as well as the bis(ylidyl)phosphanes ($Ph_3P{=}CR{-}P(Ph_3){-}CR{=}PPh_3$)[175] and bis(ylide)-substituted phosphenium ($Ph_3P{=}CR{-}P{=}CR{-}PPh_3X$) and phosphonium halides ($Ph_3P{=}CR{-}PX{-}CR{=}PPh_3$)[176] were dealt with.

The Si–P bond in silylphosphanes is cleaved by chlorinated silanes and carbosilanes. As such, in the reaction of the cyclic $(Cl_2Si{-}CH_2)_3$ with **36** in a molar ratio of 1:3 $[Me_2P(Cl)Si{-}CH_2]_3$ (**434**) is formed.[177] In the case of Si- and C-chlorinated carbosilanes the Si–P bond cleavage will not anymore be caused by the SiCl but by the CCl group, as the reaction to the ylide **435** in (135) shows. This reaction of perchlorinated carbosilanes is the entrance into the chemistry of Si-functional phosphorus ylides.



435

(135)

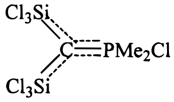
In an analogous manner $(Cl_3Si)_2CCl_2$ forms also with $LiPMe_2$ the ylide **435**, which according to (136) results in the derivative **428b** when treated with MeLi.

$$\underset{\textbf{435}}{(Cl_3Si)_2C{=}PMe_2Cl} + MeLi \rightarrow \underset{\textbf{428b}}{(Cl_3Si)_2C{=}PMe_3} + LiCl \quad (136)$$

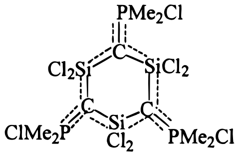
The perchlorinated 1,3,5-trisilacyclohexane $(Cl_2Si{-}CCl_2)_3$ reacts with **36** as well as with $LiPMe_2$ to the triylide **436**, which crystallizes with 1 mol of DME to $(Cl_2Si{-}C{=}PMe_2Cl)_3{\cdot}DME$.

$$(Cl_2Si{-}CCl_2)_3 + \underset{\textbf{36}}{3Me_3Si{-}PMe_2} \rightarrow \underset{\textbf{436}}{(Cl_2Si{-}C{=}PMe_2Cl)_3} + 3Me_3SiCl \quad (137)$$

An X-ray structure determination revealed that **428c** and **435** are characterized by a "propeller-like" symmetry. The atoms in the six-membered ring of **436** deviate only by 5 pm from the balanced plane. The configuration of the ylidic C atoms in **428b**, **435**, and **436** is trigonal planar. The bond angles of the ylidic C atoms in **436** just differ slightly from 120°. The Si–C and P–C bond orders amount to about 1.33 and are relatively equally distributed, which shall be expressed by means of the following kind of writing for **435** and **436**:[178]



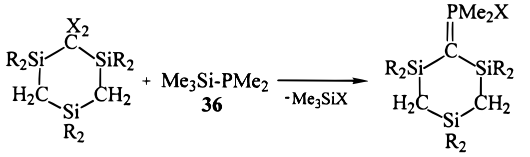
435



436

The analogous compound $(H_2Si{-}C{=}PMe_3)_3$ (**437**) could be synthesized by Schmidbaur and Zimmer-Gasser[179] from $Me_3P{=}CH{-}SiH_3$ (**438**), obtainable from PMe_3 and $ClCH_2SiH_3$. The thermally unstable silyl ylide **438** eliminates hydrogen to give **437**.

The CCl_2 moiety in linear silicon-rich carbosilanes such as $Cl_3Si{-}CH_2{-}SiCl_2{-}CCl_2{-}SiCl_3$ and $Cl_2Si(CCl_2{-}SiCl_3)_2$ also is able to cleave the Si–P bond in **36** to form the ylides $Cl_3Si{-}CH_2{-}SiCl_2{-}C({=}PMe_2Cl){-}SiCl_3$ (**435d**) and $Cl_2Si[C({=}PMe_2Cl){-}SiCl_3]_2$ (**439**), respectively. The same products were accessible in the reaction with $LiPMe_2$.[178] Also partly halogenated 1,3,5-trisilacyclohexanes with a CX_2 unit (X = Cl, Br) can be transferred into their ylidic derivatives **440**–**440b** by reacting them with **36** (138).

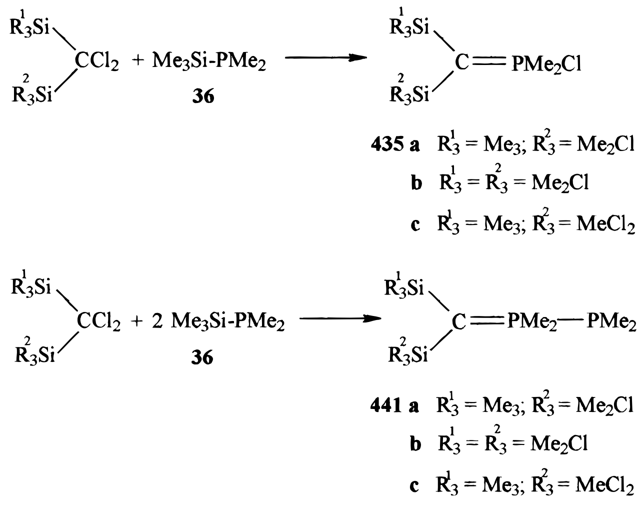


(138)

	X	R
440	Cl	Cl
440a	Cl	F
440b	Br	Me

An X-ray structure determination reveals that the atoms of the ylidic part of **440** are coplanar with shortened bond distances $d(C{-}P) = 168.6$ pm and $d(C{-}Si) = 180.1$ pm, whereas the other endocyclic Si–C distances remain nearly unaffected by the ylide formation. Only the endocyclic bond angles C–Si–C of the ylidic silicon atoms are enlarged (116°). In **440b** the distance $d(C{-}P)$ is with 164.6 pm even shorter; however, $d(P{-}Br) = 236.6$ pm is unusually large. These changes are coupled with a deviation of 17 pm for the ylidic carbon atom from the ylide plane. The other distances and angles in the Si-methylated six-membered ring are normal. The ring in **440b** has a

Scheme 31



boat conformation; in **440**, a flat chair conformation.[180]

B. Influence of the Substituents in $(R_3Si)_2CX_2$ with R = Me, Cl and X = Br on Formation and Reactions of the Ylides

The Si−P bond cleavage in the silylphosphanes as well as the ylide formation at the dichlorinated carbon of the 1,3-disilapropanes depends on the extent of silicon chlorination. Whereas $(Cl_3Si)_2CCl_2$ with **36** forms already at −15 °C the crystalline $(Cl_3Si)_2C{=}PMe_2Cl$ (**435**) in 77% yield (135),[178] the methylated $(Me_3Si)_2CCl_2$ reacts with **36** in a molar ratio of 1:1 only at 75 °C (15 h) in a sealed tube without solvent. The ylides which were obtained by successive substitution of the methyl groups by chlorine atoms in the 1,3-disilapropanes are shown in Scheme 31.

A detailed insight into the ylide synthesis could be gained by investigating the quantitatively proceeding reaction of $(ClMe_2Si)_2CCl_2$ with **36** (139−141) yielding the ylide **441b** via the isolable intermediate $(ClMe_2Si)_2C{=}PMe_2Cl$ (**435b**).[181]

$$(\mathrm{ClMe_2Si})_2\mathrm{CCl_2} \xrightarrow[-2\mathrm{Me_3SiCl}]{2\mathrm{Me_3Si{-}PMe_2}} \underset{\mathbf{441b}}{(\mathrm{ClMe_2Si})_2\mathrm{C{=}PMe_2{-}PMe_2}} \quad (139)$$

$$\underset{\mathbf{441b}}{(\mathrm{ClMe_2Si})_2\mathrm{C{=}PMe_2{-}PMe_2}} \xrightarrow{(\mathrm{ClMe_2Si})_2\mathrm{CCl_2}} \underset{\mathbf{435b}}{2(\mathrm{ClMe_2Si})_2\mathrm{C{=}PMe_2Cl}} \quad (140)$$

$$\underset{\mathbf{435b}}{(\mathrm{ClMe_2Si})_2\mathrm{C{=}PMe_2Cl}} \xrightarrow{\mathrm{Me_3Si{-}PMe_2}} \underset{\mathbf{441b}}{(\mathrm{ClMe_2Si})_2\mathrm{C{=}PMe_2{-}PMe_2}} \quad (141)$$

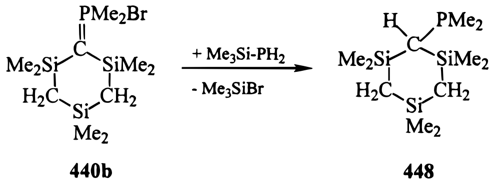
A similar dependence of the reactivity from the extent of chlorination can be found with monosilanes. Whereas the chlorine atom in $Me_3Si{-}CH_2Cl$ will be substituted by $LiPMe_2$ to form $Me_3Si{-}CH_2{-}PMe_2$ (**442**), and $Cl_3Si{-}CH_2Cl$ with **36** yields $(Me_2P)Cl_2Si{-}CH_2Cl$ (**443**), $Cl_3Si{-}CCl_3$ reacts with $LiPMe_2$ to give the ylide **444** (142).[178]

$$\mathrm{Cl_3Si{-}CCl_3} + \mathrm{LiPMe_2} \xrightarrow[-\mathrm{LiCl}]{} \underset{\mathbf{444}}{(\mathrm{Cl_3Si})(\mathrm{Cl})\mathrm{C{=}PMe_2Cl}} \quad (142)$$

Compared to the chlorinated compounds $(R_3Si)_2CCl_2$ or $(R_3Si)_2C{=}PMe_2Cl$, the bromine derivatives are considerably more reactive. Whereas at 20 °C no reaction of $(Me_3Si)_2CCl_2$ with **36** can be observed, the brominated compound $(Me_3Si)_2CBr_2$ will give the ylide **445** in 90% yield (143) without any indication for $(Me_3Si)_2C{=}PMe_2{-}PMe_2$ (**441**).

$$(\mathrm{Me_3Si})_2\mathrm{CBr_2} + \underset{\mathbf{36}}{\mathrm{Me_3Si{-}PMe_2}} \xrightarrow[-\mathrm{Me_3SiBr}]{} \underset{\mathbf{445}}{(\mathrm{Me_3Si})_2\mathrm{C{=}PMe_2Br}} \quad (143)$$

In the reaction with $Me_3Si{-}PH_2$ (**59**) or $(Me_3Si)_2PH$ (**79**), the PBr unit in $(Me_3Si)_2C{=}PMe_2Br$ (**445**) spontaneously cleaves the Si−P bond at 0 °C, yielding the phosphane $(Me_3Si)_2C(H)PMe_2$ (**446**), the formation of which in the case of **59** can be assumed via the phosphino-substituted ylide $(Me_3Si)_2C{=}PMe_2{-}PH_2$ (**447**). The reaction of the ylidic cycle **440b** proceeds quite analogously.



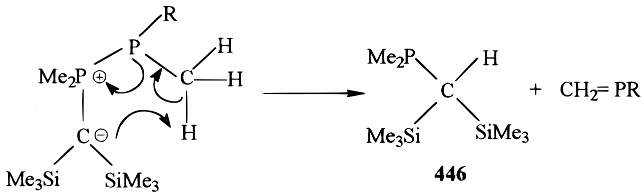
(144)

The less reactive silylphosphane **32** initially forms the ylide **449** with the P−P unit in 95% yield (145), which decomposes by thermal treatment to the phosphane **446** (Scheme 32).

$$\underset{\mathbf{445}}{(\mathrm{Me_3Si})_2\mathrm{C{=}PMe_2Br}} + \underset{\mathbf{32}}{(\mathrm{Me_3Si})_2\mathrm{PMe}} \xrightarrow[-\mathrm{Me_3SiBr}]{} \underset{\mathbf{449}}{(\mathrm{Me_3Si})_2\mathrm{C{=}PMe_2{-}P(Me)SiMe_3}} \quad (145)$$

Investigations using $(Me_3Si)_2C{=}PMe_2{-}P(CD_3)SiMe_3$ (**449a**) confirmed that the deuterium in $(Me_3Si)_2C(D)PMe_2$ (**446a**) originates from the $P(CD_3)SiMe_3$ unit of **449a**, so the rearrangement can be described as demonstrated in Scheme 32.[181]

Scheme 32



441 R = Me
449 R = SiMe3

Compared to the more reactive $(Me_3Si)_2CBr_2$, the chlorine derivative $(Me_3Si)_2CCl_2$ reacts with **36** only

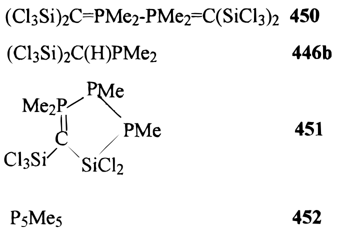
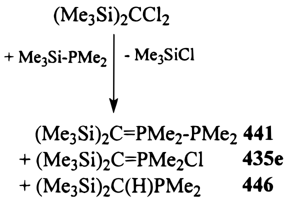


Figure 30. Products from the reaction of $(Me_3Si)_2PMe$ (**32**) with $(Cl_3Si)_2C{=}PMe_2Cl$ (**435**).

at 75 °C, forming the compounds **441, 435e**, and **446** in a ratio of 2:1:1 (146).



(146)

When keeping the mixture at this temperature, **441** is completely consumed after 50 h. A separate synthesis by reacting $(Me_3Si)_2CCl_2$ with 2 mol of **36** yields white crystals of the ylide **441**, which are decomposed to **446** by thermal treatment (147).[181]

$$\underset{\mathbf{441}}{(Me_3Si)_2C{=}PMe_2{-}PMe_2} \rightarrow \underset{\mathbf{446}}{(Me_3Si)_2C(H)PMe_2} + \text{“}MeP{=}CH_2\text{”} \quad (147)$$

Tough conditions (sealed tube, 130 °C, 15 h) are necessary for the reaction of **32** with $(Cl_3Si)_2C{=}PMe_2Cl$ (**435**). The course of this reaction incorporates a number of stages from which the compounds in Figure 30 could be isolated.

The diylide **450** crystallized from the reaction mixture. The other three products were separated from remaining **435** by fractionated sublimation. ^{31}P NMR investigations indicate the reaction according to (148) to be the initial step.

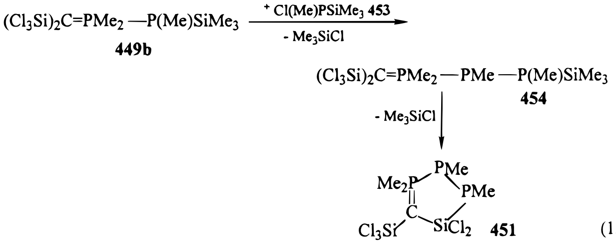
$$\underset{\mathbf{435}}{(Cl_3Si)_2C{=}PMe_2Cl} + \underset{\mathbf{32}}{MeP(SiMe_3)_2} \xrightarrow[-Me_3SiCl]{} \underset{\mathbf{449b}}{(Cl_3Si)_2C{=}PMe_2{-}P(Me)SiMe_3} \quad (148)$$

Starting from **449b** the formation of **450** probably is caused by **435** (149).

$$\underset{\mathbf{449b}}{(Cl_3Si)_2C{=}PMe_2{-}P(Me)SiMe_3} + \underset{\mathbf{435}}{(Cl_3Si)_2C{=}PMe_2Cl} \rightarrow \underset{\mathbf{450}}{(Cl_3Si)_2C{=}PMe_2{-}PMe_2{=}C(SiCl_3)_2} + \underset{\mathbf{453}}{Cl(Me)P{-}SiMe_3} \quad (149)$$

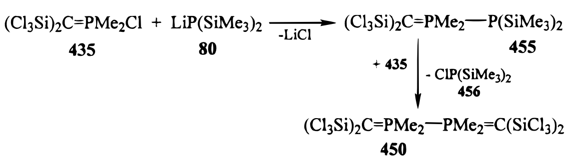
The additionally generated silylphosphane **453** explains the formation of P_5Me_5 (**452**) as well as of the five-membered ring **451**. It eliminates Me_3SiCl, yielding “MeP” (analogous to “*t*BuP”[182]), which can recombine to P_5Me_5. This assumption is supported by the reaction of **32** with Br_2, resulting in P_5Me_5 and Me_3SiBr.

Compound **453** is also responsible for the formation of the ylide **454** and its subsequent cyclization to **451** according to (150).



(150)

Another possibility for synthesizing compound **450** is given in (151).[183]

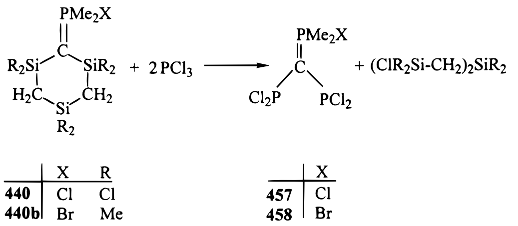


(151)

The reaction of **32** with **435** reveals that unexpected compounds appearing at higher temperatures were produced via a sequence of steps which can be attributed to known basic reactions.

C. Reactions of Silylated Phosphorus Ylides with PCl3

The Lewis acid PCl_3 cleaves the C−Si bond at the ylidic carbon atom in silylated phosphorus ylides, as shown in (152).



(152)

The reaction between the linear ylide **435** and PCl_3 proceeds quantitatively already at 0 °C in benzene to **457** (mp, 84 °C), which can be isolated due to the volatility of $SiCl_4$ (153), in contrast to the previously mentioned reaction.[184]

$$\underset{\mathbf{435}}{(Cl_3Si)_2C{=}PMe_2Cl} + 2PCl_3 \rightarrow \underset{\mathbf{457}}{(Cl_2P)_2C{=}PMe_2Cl} + 2SiCl_4 \quad (153)$$

In an analogous manner the Me_3Si units in $(Me_3Si)_2C{=}PMe_3$ (**428**) can be replaced by the PCl_2 group generating $(Cl_2P)_2C{=}PMe_3$ (**459**).[185]

D. Phosphinophosphinidene Phosphoranes

The formation and stability of the phosphinophosphinidene phosphoranes were determined by conditions of syntheses and also by the substituents on the

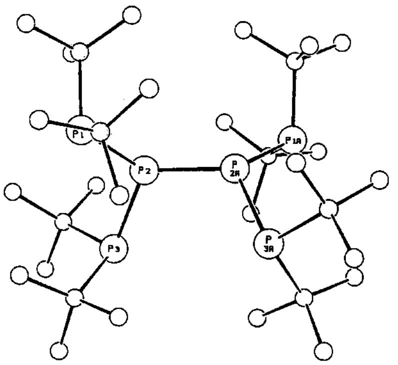


Figure 31. Molecular structure of the hexaphosphane $(tBu_2P)_2P{-}P(PtBu_2)_2$. Reprinted with permission from ref 103. Copyright 1992 Wiley-VCH Verlag GmbH.

phosphorus atom of the basic compounds, the lithiated triphosphanides. In investigations in analyzing the molecular structures, an additional SCF calculation gives more information.

1. Syntheses of Phosphinophosphinidene Phosphoranes

Investigations in the syntheses of phosphorus-rich phosphanes afforded the triphosphane $(tBu_2P)_2P(SiMe_3)$ (**236**), the metalation of which with BuLi by cleaving the Si−P bond forms the lithiated triphosphanide $Li(THF)_2[\eta^2\text{-}(tBu_2P)_2P]$ (**268**).[85,186] With 1,2-dibromoethane, **268** reacts to the phosphinophosphinidene phosphorane $tBu_2P{-}P{=}P(Br)tBu_2$ (**460**).[187] Studies of this reaction at different temperatures and conditions reveal that beside **460** also the hexaphosphane $(tBu_2P)_2P{-}P(PtBu_2)_2$ and tBu_2PBr as well as the cyclophosphanes $P_3(PtBu_2)_3$ (**287**) and $P_4(PtBu_2)_4$ (**288**) were obtained. A metal−halogen exchange induces reaction (154), followed by the fast proceeding transformation to the ylide **460**. According to (156) the hexaphosphane $(tBu_2P)_2P{-}P(PtBu_2)_2$ could only be observed if an excess of **268** was used.

$$\underset{\mathbf{268}}{Li(THF)_2[\eta^2\text{-}(tBu_2P)_2P]} + BrCH_2{-}CH_2Br \rightarrow (tBu_2P)_2PBr + C_2H_4 + LiBr \quad (154)$$

$$(tBu_2P)_2PBr \rightarrow \underset{\mathbf{460}}{tBu_2P{-}P{=}P(Br)tBu_2} \quad (155)$$

$$(tBu_2P)_2PBr + \underset{\mathbf{268}}{Li(THF)_2[\eta^2\text{-}(tBu_2P)_2P]} \rightarrow (tBu_2P)_2P{-}P(PtBu_2)_2 + LiBr \quad (156)$$

The ^{31}P NMR spectrum recorded at −70 °C immediately after the formation of the ylide **460** shows its signals as the main product **460** and only traces of the brominated triphosphane. NMR measurements at various temperatures of a pure solution of **460** in toluene showed at −70 °C exclusively the signals of **460**. On warming to −20 °C signals of $(tBu_2P)_2PBr$ were additionally observed in small concentration, and at 20 °C **460** decomposes to tBu_2PBr and the phosphinidene $tBu_2P{-}P$, which reacts on to yield the cyclophosphanes **287** and **288**. The hexaphosphane $(tBu_2P)_2P{-}P(PtBu_2)_2$, the molecular structure of which is shown in Figure 31,[103] does not result from the pure solution of **460**, instead from the reaction of the ylide **460** with **268** (157).[188]

$$\underset{\mathbf{460}}{tBu_2P{-}P{=}P(Br)tBu_2} + \underset{\mathbf{268}}{Li(THF)_2[\eta^2\text{-}(tBu_2P)_2P]} \rightarrow (tBu_2P)_2P{-}P(PtBu_2)_2 + LiBr \quad (157)$$

The formation of the phosphinophosphinidene phosphoranes is considerably determined by the substituents on the primary phosphorus atom of the triphosphanide. The bromination of **222** with 1,2-dibromoethane leads to the triphosphane **461** by a metal−halogen exchange (158).

$$\underset{\mathbf{222}}{tBu_2P{-}P(Li){-}P(SiMe_3)_2} + BrCH_2{-}CH_2Br \xrightarrow[-C_2H_4]{-LiBr} \underset{\mathbf{461}}{tBu_2P{-}P(Br){-}P(SiMe_3)_2} \quad (158)$$

At −20 °C, **461** can be stored for months, but at 20 °C it decomposes during a few hours, forming the phosphanes tBu_2PBr, tBu_2PH and $(Me_3Si)_2PH$ (**87**).[189]

In contrast to this observation the chlorinated $tBu_2P{-}P(Cl){-}P(SiMe_3)_2$ (**221a**) eliminates Me_3SiCl at 20 °C and generates the cyclotetraphosphane $P_4[PtBu_2]_2[SiMe_3]_2$ (**282**) via the triphosphene $tBu_2P{-}P{=}P{-}SiMe_3$ (**462**).[101] Already at −70 °C $tBu(Me_3Si)P{-}P(Li){-}PtBu_2$ (**463**) reacts with CH_3Cl, yielding $tBu(Me_3Si)P{-}P{=}P(Me)tBu_2$ (**464**). However with 1,2-dibromoethane it forms $tBu(Me_3Si)P{-}P(Br){-}PtBu_2$ (**465**) as the main product besides $tBu(Me_3Si)P{-}P{=}P(Br)tBu_2$ (**466**).[190a] Also a salt elimination proceeds in the reaction of the phosphanide **222** with CH_3Cl to generate the triphosphane $tBu_2P{-}P(Me){-}P(SiMe_3)_2$ (**222a**), but no rearrangement to the corresponding ylide could be observed.[190b]

The Si−P bond in $[(F_3C)_2P]_2P{-}SiMe_3$ (**467**) cannot be cleaved, not even by BuLi.[189] The direct way via the Si−P bond cleavage in $(tBu_2P)_2P(SiMe_3)$ (**236**) with different halogenating agents, such as for instance *N*-bromosuccinimide (NBS) (159), offers another possibility for synthesizing the phosphinophosphinidene phosphorane **460**.

$$\underset{\mathbf{236}}{(tBu_2P)_2P{-}SiMe_3} + NBS \rightarrow \underset{\mathbf{460}}{tBu_2P{-}P{=}P(Br)tBu_2} \quad (159)$$

Analogously, both compounds $tBu_2P{-}P{=}P(X)tBu_2$ (X = Cl (**467**), I (**468**)) were accessible. These halogenations proceed independently from the lithium phosphanide **268** and demonstrate that it is not a necessary requirement for the formation of ylides.[191]

In the reactions of $Li(THF)_2[\eta^2\text{-}(tBu_2P)_2P]$ (**268**) with different alkylhalogenides between −70 °C and +20 °C in THF or pentane besides the ylidic compounds, also the corresponding triphosphanes were obtained (160). In THF the phosphinophosphinidene phosphoranes are predominantly formed. In the case

Table 16. $^{31}P\{^1H\}$ NMR Data of the Phosphinophosphinidene Phosphoranes 469a–f and Related Triphosphanes[a]

R		$\delta(^{31}P)$ (ppm)			J (Hz)		
		P^1	P^2	P^3	$J_{(1,2)}$	$J_{(2,3)}$	$J_{(1,3)}$
$tBu_2P^3{-}P^2{=}P^1(R)tBu_2$	**469**						
Me	**a**	57.49	−204.73	31.98	−596.7	−274.8	63.7
Et	**b**	61.14	−190.73	28.64	−618.5	−292.5	54.8
*n*Pr	**c**	59.85	−188.56	27.89	−620.4	−290.3	54.7
*n*Bu	**d**	56.93	−197.13	23.23	−610.3	−278.8	52.9
CH_2Ph	**e**	62.82	−181.70	30.36	−630.2	−288.6	50.6
CF_3	**f**	90.99	−186.51	14.22	−722.7	−275.1	67.6
$[tBu_2P^1]_2P^2R$							
Me		38.56	−65.76		−291.4		
Et		45.61	−45.01		−335.7		
*n*Pr		45.85	−52.53		−334.2		
*i*Pr		44.09	−39.54		−460.9		
*n*Bu		40.6	−54.4		−327.0		
CH_2Ph		47.87	−46.96		−348.3		
$CH_2{-}CH{=}CH_2$		46.40	−52.25		−324.6		

[a] In toluene-d_8/THF at −70 °C

of R = *i*Pr or $CH_2{=}CH{-}CH_2$, respectively, the triphosphanes resulted exclusively. The ^{31}P NMR data of the described compounds are listed in Table 16.[192]

$$\underset{\mathbf{268}}{2\,Li(THF)_2[\eta^2\text{-}(tBu_2P)_2P]} + 2\,RX \longrightarrow \underset{\mathbf{469a\text{-}f}}{tBu_2P{-}P{=}P(R)tBu_2} + (tBu_2P)_2PR + 2\,LiX \qquad (160)$$

X = Cl, Br

469	a	b	c	d	e	f
R	Me	Et	*n*Pr	*n*Bu	$PhCH_2$	CF_3

The reactions of the phosphinophosphinidene phosphorane **460** with RLi (R = Me, *n*Bu, *t*Bu) lead to the alkylated products **469(a,d,g)** as well as to the corresponding triphosphanes $(tBu_2P)_2PR$ (R = H in case of *t*BuLi) in different ratios. Whereas the phosphinidene **469a** results as the main product with MeLi, with *n*BuLi or *t*BuLi compound **469d** or **469g** (R = *t*Bu) can be isolated only as a side product. The formation of the protonated triphosphane $(tBu_2P)_2PH$ corresponds to the general behavior of sterically loaded *t*Bu compounds, which readily eliminate $Me_2C{=}CH_2$. Other examples are the reactions of $PtBu_3$ with *t*BuX (X = halogen), yielding $tBu_3PH^+X^-$ [193] as well as the formation of tBu_2SiHCl and isobutene from $tBuSiCl_3$ and *t*BuLi.[194]

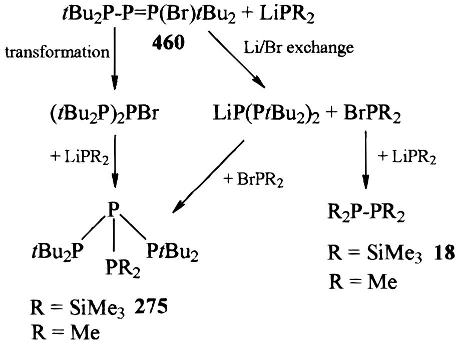
Similarly **268** with *t*BuCl at −70 °C exclusively yields $(tBu_2P)_2PH$ according to (161).

$$\underset{\mathbf{268}}{Li(THF)_2[\eta^2\text{-}(tBu_2P)_2P]} + tBuCl \rightarrow (tBu_2P)_2PH + Me_2C{=}CH_2 + LiCl \qquad (161)$$

The alcoholysis of **460** at −70 °C leads to $(tBu_2P)_2PH$ and tBu_2PH. As shown in Scheme 33, with the lithiumphosphanides $LiPR_2$ (R = $SiMe_3$ (**80**), Me) finally the diphosphanes $R_2P{-}PR_2$ (R = $SiMe_3$ (**185**), Me) and isotetraphosphanes $P(PtBu_2)_2PR_2$ (R = $SiMe_3$ (**275**), Me) result.[195]

Reactions between **460** and the phosphanes PR_3 (162) even after longer times remain incomplete; anyway the homogeneous solutions contain no other compounds.

Scheme 33



$$\underset{\mathbf{460}}{tBu_2P{-}P{=}P(Br)tBu_2} + PR_3 \longrightarrow \underset{\mathbf{470a\text{-}g}}{tBu_2P{-}P{=}PR_3} + tBu_2PBr \qquad (162)$$

470	a	b	c	d	e	f	g
R_3	Et_3	tBu_3	Ph_3	$(NMe_2)_3$	$(NEt_2)_3$	$(NEt_2)_2Me$	$(SiMe_3)Me_2$

In an analogous way to (162) the different chlorinated phosphinophosphinidene phosphoranes $tBu_2P{-}P{=}P(Cl)R_2$ (**471a–c**) are accessible by treating **460** with the chlorophosphanes R_2PCl (R_2 = tBu_2, *t*BuPh, $(NEt_2)_2$). However with other halogenophosphanes as Ph_2PCl, e.g. besides the phosphinophosphinidene phosphorane **471d** already at −70 °C, additional products resulted. $(CF_3)_2PBr$ reacts with **460** to give $(CF_3)_2P{-}P{=}P(Br)tBu_2$ (**472**), $tBu_2P{-}P{=}P(Br)(CF_3)_2$ (**473**), and further compounds. With di- and trichlorinated phosphanes as $tBuPCl_2$ or PCl_3, respectively, only decomposition products were found. In Table 17 the described ylidic compounds with their NMR data are summarized.[196]

2. Influence of the Substituents R in the Triphosphanes $(R_2P)_2P{-}SiMe_3$ and Phosphanides $Li(THF)_2[\eta^2\text{-}(R_2P)_2P]$ (R = Ph, NEt_2, iPr, tBu) on the Formation and Properties of the Phosphinophosphinidene Phosphoranes

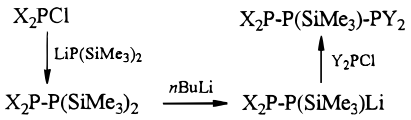
Most of the previously described phosphinophosphinidene phosphoranes contained *tert*-butyl groups

Table 17. $^{31}P\{^{1}H\}$ NMR Data of the Ylides $tBu_2P{-}P{=}PR_3$ (470a−g), $tBu_2P{-}P{=}P(Cl)R_2$ (471a−d), $tBu_2P{-}P{=}P(Br)(CF_3)_2$ (473), and $(CF_3)_2P{-}P{=}P(Br)tBu_2$ (472)

compd		$\delta(^{31}P)$ (ppm)			J [Hz]			
		P^1	P^2	P^3	$J_{(1,2)}$	$J_{(2,3)}$	$J_{(1,3)}$	$J_{(P,F)}$
$tBu_2P^3{-}P^2{=}P^1R_3$	**470**							
$R_3 = Et_3$[b]	**a**	40.40	−224.85	24.98	−518.5	−240.2	90.9	
$R_3 = tBu_3$[a]	**b**	74.91	−178.16	26.58	−670.2	−302.3	39.9	
$R_3 = Ph_3$[a]	**c**	13.60	−181.25	36.34	−565.2	−238.9	96.6	
$R_3 = (NMe_2)_3$[c]	**d**	103.26	−182.36	19.6	−577.3	−246.7	110.6	
$R_3 = (NEt_2)_3$[c]	**e**	106.83	−183.24	25.03	−584.9	−263.2	117.0	
$R_3 = (NEt_2)_2Me$	**f**	93.52	−176.65	23.65	−534.1	−242.2	119.4	
$R_3 = Me_2(SiMe_3)$[b]	**g**	−34.29	−191.32	23.73	−536.2	−250.1	71.9	
$tBu_2P^3{-}P^2{=}P^1(Cl)R_2$	**471**							
$R_2 = tBu_2$[a]	**a**	157.51	−124.35	15.54	−697.0	−252.3	40.3	
$R_2 = tBuPh$[a]	**b**	142.57	−136.30	22.34	−667.0	−228.9	87.2	
$R_2 = (NEt_2)_2$[a]	**c**	121.99	−118.27	16.48	−677.6	−231.0	122.0	
$R_2 = Ph_2$	**d**	97.45	−117.43	12.01	−619.1	−207.1	100.3	
$(CF_3)_2P{-}P{=}P(Br)tBu_2$	**472**	152.38	−153.02	19.27	−585.9	−283.8	71.3	62.5
$tBu_2P{-}P{=}(Br)(CF_3)_2$	**473**	60.94	−251.19	32.96	−558.6	−412.8	20.3	86.4

[a] In toluene-d_8/THF at −70 °C. [b] Without THF. [c] In toluene-d_8 at −30 °C.

Scheme 34



and preferably a bromine or the methyl substituent at the ylidic phosphorus atom. To study the influence of the substituents on formation and properties of the phosphinophosphinidene phosphoranes, the silylated triphosphanes $X_2P{-}P(SiMe_3){-}PY_2$ **474**−**478** and the phosphanides $Li(THF)_2[X_2P{-}P{-}PY_2]$ **479**−**483** were synthesized. The triphosphanes **474**−**478** were treated with CBr_4; the lithium phosphanides, with 1,2-dibromoethane or MeCl, respectively, at −70 °C. The syntheses of the compounds **474**−**478** were realized according to the building principle shown in Scheme 34.[83,84] Metalation by means of *n*BuLi afforded the corresponding phosphanides **479**−**483** (163).

$$\begin{array}{ll}
X_2P{-}P(SiMe_3){-}PY_2 + nBuLi \rightarrow & \\
X_2 = iPr_2,\ Y_2 = tBu_2 & \mathbf{474} \\
X_2 = Y_2 = (tBu)Ph & \mathbf{475} \\
X_2 = tBu_2,\ Y_2 = Ph_2 & \mathbf{476} \\
X_2 = Y_2 = Ph_2 & \mathbf{477} \\
X_2 = tBu_2,\ Y_2 = (NEt_2)_2 & \mathbf{478}
\end{array}$$

$$\begin{array}{l}
Li(THF)_2[X_2P{-}P{-}PY_2] + nBuSiMe_3 \quad (163) \\
\mathbf{479} \\
\mathbf{480} \\
\mathbf{481} \\
\mathbf{482} \\
\mathbf{483}
\end{array}$$

The ^{31}P NMR data of the silylated triphosphanes **474**−**478** and their ylidic products from the reactions with CBr_4 as well as of the phosphanides $Li(THF)_2[X_2P{-}P{-}PY_2]$ (**479**−**483**) and the resulting compounds from reactions with 1,2-dibromoethane or MeCl are summarized in Table 18.

In summary it may be established that the substituents in the starting compounds **474**−**478** and **479**−**483**, respectively, have an influence on (a)the choice of either ylide or triphosphane as the main product as well as on the position of the ylidic P atom, (b)the stability of the ylides, and (c) the formation of secondary products.

(a) The *t*Bu group favors the formation of ylides. The *t*Bu-substituted P atom will be the ylidic center and therefore add a Br atom or a Me group, which, however, is added to P(2) in the case of the resulting triphosphanes. With the introduction of a *i*Pr or Ph group the tendency to form ylides decreases. The NEt_2 units in **483** override the dominating influence of the *t*Bu group with the consequence that the ylide is formed at the $P(NEt_2)_2$ group $\{P{=}P(Br)(NEt_2)_2;\ P{=}P(Me)(NEt_2)_2\}$; however, the triphosphane $tBu_2P{-}P(Me){-}P(NEt_2)_2$ is the main product with 94% yield. With brominating agents the phosphane **474** and the phosphanide **479** (X = *i*Pr, Y = *t*Bu) form the ylidic center at the Y-substituted phosphorus atom, whereas with MeCl both the X- and the Y-substituted phosphorus are employed.

(b) The brominated ylides are less stable than the corresponding methyl-substituted ylides. Within the group of the bromine derivatives, the stability increases in the following order: $iPr_2P{-}P{=}P(Br)iPr_2$ (**496**) < $iPr_2P{-}P{=}P(Br)tBu_2$ (**484**) < $PhtBuP{-}P{=}P(Br)PhtBu$ (**487**) < **460**, but above −30 °C they all decompose. With 1,2-dibromoethane $Li(THF)_2[(iPr_2P)_2P]$ (**497**) generates only traces of the ylide **496** in addition to the hexaphosphane $(iPr_2P)_2P{-}P(PiPr_2)_2$ as the main product.[104] With MeCl in THF $iPr_2P{-}P{=}P(Me)iPr_2$ (**498**) and $(iPr_2P)_2PMe$ were isolated in a molar ratio of 1:1. The phosphanes tBu_2PBr and iPr_2PBr result as the main products in the reaction of **474** with CBr_4 in addition to small amounts of $iPr_2P{-}P{=}P(Br)tBu_2$ (**484**) and $(iPr_2P)_2PBr$, whereas from the corresponding $Li(THF)_2[iPr_2P{-}P{-}PtBu_2]_2$ (**479**) with MeCl the compounds $iPr_2P{-}P{=}P(Me)tBu_2$ (**485**), $tBu_2P{-}P{=}P(Me)iPr_2$ (**486**), and $iPr_2P{-}P(Me){-}PtBu_2$ could be isolated in a molar ratio of 5:4:1. In the corresponding methylation of **481** the ylide $Ph_2P{-}P{=}P(Me)tBu_2$ (**491**) and the triphosphane $Ph_2P{-}P(Me){-}PtBu_2$ were accessible in a molar ratio of 5:3.

(c) In the case of the phenyl-substituted triphosphanes $R_2P{-}P(SiMe_3){-}PPh_2$ (R = *t*Bu (**476**), Ph (**477**)) only traces of the phosphinidenes were found.

Table 18. ^{31}P{^{1}H} NMR Data of the Triphosphanes X$_2$P−P(SiMe$_3$)−PY$_2$ (474−478) Phosphanides Li(THF)$_2$[X$_2$P−P−PY$_2$] (479−483) and Products from the Reactions with CBr$_4$, 1,2-Dibromoethane and MeCl[a]

compd		δ(^{31}P) (ppm)			J (Hz)		
		P^1	P^2	P^3	$J_{(1,2)}$	$J_{(2,3)}$	$J_{(1,3)}$
X$_2$P^3−P^2(SiMe$_3$)−P^{1}Y$_2$							
*i*Pr$_2$P−P(SiMe$_3$)−P*t*Bu$_2$	**474**	13.27	−152.74	40.92	−404.4	−430.6	
Ph*t*BuP−P(SiMe$_3$)−P*t*BuPh	**475**	1.68	−136.37	1.68		−374.7	
*t*Bu$_2$P−P(SiMe$_3$)−PPh$_2$	**476**	−20.69	−130.0	39.07	−329.9	−407.4	
Ph$_2$P−P(SiMe$_3$)−PPh$_2$	**477**	−24.66	−119.79	−24.66		−199.1	
*t*Bu$_2$P−P(SiMe$_3$)−P(NEt$_2$)$_2$	**478**	111.47	−141.86	45.60	−137.6	−430.1	72.1
Li(THF)$_2$[X$_2$P^3−P^2−P^{1}Y$_2$]							
Li(THF)$_2$[*i*Pr$_2$P−P−P*t*Bu$_2$]	**479**	62.67	−157.67	33.48	−318	−312	300
Li(THF)$_2$[(Ph*t*BuP)$_2$P]	**480**	37.91	−168.28	37.91		−306.8	
Li(THF)$_2$[*t*Bu$_2$P−P−PPh$_2$]	**481**	12.27	−131.76	61.55	−340.5	−323.8	289.1
Li(THF)$_2$[(Ph$_2$P)$_2$P]	**482**	5.39	−112.06	5.39		−348.3	
Li(THF)$_2$[*t*Bu$_2$P−P−P(NEt$_2$)$_2$]	**483**	158.43	−126.96	51.26	−307.5	−284.0	329.5
reaction products							
*i*Pr$_2$P^3−P^2=P^1(Br)*t*Bu$_2$	**484**	146.06	−97.73	11.7	−631.2	−229.6	64.7
*i*Pr$_2$P−P=P(Me)*t*Bu$_2$	**485**	59.43	−217.89	5.01	−570.8	−255.7	57.4
*t*Bu$_2$P−P=P(Me)*i*Pr$_2$	**486**	45.12	−215.32	14.95	−550.8	−252.0	78.0
Ph*t*BuP−P=P(Br)Ph*t*Bu	**487**	151.89	−133.49	−0.26	−623.4	−208.0	118.0
Ph*t*BuP−P=P(Me)Ph*t*Bu	**488**	50.57	−212.67	2.27	−527.2	−234.5	92.5
Ph*t*BuP−P=P(Et)Ph*t*Bu	**489**	55.53	−234.50	1.61	−533.1	−238.3	82.1
Ph$_2$P−P=P(Br)*t*Bu$_2$	**490**	157.58	−102.20	−19.28	−637.1	−246.6	63.3
Ph$_2$P−P=P(Me)*t*Bu$_2$	**491**	58.66	−181.92	−15.82	−542.3	−263.1	68.3
Ph$_2$P−P=P(Br)Ph$_2$	**492**	85.97	−137.9	*b*	−563.6	−213.5	100.2
*t*Bu$_2$P−P=P(Br)(NEt$_2$)$_2$	**493**	122.87	−87.79	22.30	−693.0	−240.0	136.5
*t*Bu$_2$P−P=P(Me)(NEt$_2$)$_2$	**494**	93.52	−176.65	23.65	−534.1	−242.2	119.4
*t*Bu$_2$P−P=P(H)(NEt$_2$)$_2$	**495**	87.93	−196.84	27.71	−534.2	−225.8	166.4

[a] In toluene-d_8/THF at −70 °C; **490**, **491** in toluene-d_8 at −70 °C. [b] Unresolved superimposed multiplets.

Table 19. P−P Distances (pm) and Bonding Angles (deg) of the Phosphinophosphinidene Phosphoranes *t*Bu$_2$P3−P2=P1(X)*t*Bu$_2$ (X = Br (460), Me (469a)) and *t*Bu(Me$_3$Si)P3−P2=P1(Me)*t*Bu$_2$ (464)[a]

	460	464	469a
P1−P2	207.7(2) [211]	213.58(5)	212.63(4) [217]
P2−P3	220.2(2) [223]	218.26(5)	217.91(4) [222]
P1−X[b]	229.4(1) [231]	181.7(2)	181.20(10) [183]
P1−C3[c]	188.9(5) [191]	188.2	188.48 [190]
P1−C2[c]	188.2(5) [191]	188.06(14)	187.90(11) [190]
P3−C4[d]	190.8(5) [192]	192.65	191.10 [193]
P1−P2−P3	105.77(7) [107]	100.29(2)	100.95(3) [102]
P2−P1−X[b]	113.56(6) [116]	115.56	115.92 [115][e]

[a] Values in square brackets are calculated data. [b] X in **460**, Br; X in **464** and **469a**, Me. [c] On the ylidic C atom. [d] On the P(*t*Bu$_2$) group. [e] For both conformers.

Instead, with CBr$_4$ the phosphanes *t*Bu$_2$PBr and *t*Bu$_2$PH from **476** and the diphosphane Ph$_2$P−PPh$_2$ in the case of **477** were isolated as the main products.[197]

3. Molecular Structures and Bonding Properties of tBu$_2$P–P=P(X)tBu$_2$ (X = Br, Me) and tBu(Me$_3$Si)P–P=P(Me)tBu$_2$

The crystals of **460** were isolated from pentane at −70 °C. They are thermochromic, yellow at −70 °C, and colorless at −120 °C. Solutions in toluene, pentane, or THF are yellow. Compound **460** crystallizes in the monoclinic space group $P2_1/c$ with a = 2888.9(3) pm, b = 972.16(10) pm, c = 1534.04(14) pm, β = 105.13(8)°, and 8 formula units in the unit cell. The two independent P$_3$ units form angles of 105.77 or 105.98°, respectively.[198] In Table 19 the P−P distances and bonding angles of the three phosphinophosphinidene phosphoranes **460**, **464**, and **469a** are summarized. Compound **469a** resulted from treating Li(THF)$_2$[η^2-(*t*Bu$_2$P)$_2$P] (**268**) with Me$_2$SO$_4$ or CH$_3$Cl, respectively.[199]

The three phosphorus atoms in all of these compounds form an angle, which differs by only 0.66° between **469a** and **464**, however, by 5.48° between **460** and **464**. While in **460** the P1−P2 distance with 207.7 pm corresponds to a P=P double bond and the other P2−P3 distance with 220.2 pm to a single bond (difference 12.5 pm), the differences of the P−P distances in **469a** (5.28 pm) and **464** (4.68 pm) are much smaller. The molecular structures of the three compounds are shown in Figure 32; the ^{31}P NMR data are summarized in Table 20.

An ab initio SCF calculation resulted in P−P bond distances of 3−4 pm and P−C bond distances of 1−2 pm longer than the experimental ones determined by X-ray structure analysis.[199]

The bonding situation in **460** and **469a** can be understood as a result of mixing the valence structures **I** and **II**.

$$\underset{\textbf{I}}{\mathrm{R_2P3{-}P2(^{-}){-}P1(^{+})(X)R_2}} \leftrightarrow \underset{\textbf{II}}{\mathrm{R_2P3{-}P2{=}P1(X)R_2}}$$

This corresponds to the delocalization of a lone pair of P2 into low-lying orbitals of P1. In any case a single bond is expected for P3−P2, whereas P2−P1 is stabilized by Coulomb interactions or by covalent partial double bonds. In both cases (for X = Br and Me), a delocalization of the P2 lone pair in the direction of P1 is observed, which is characterized by the polarized 3pπ bond P2 → P1. The degree of delocalization is increased in the Br derivative, but

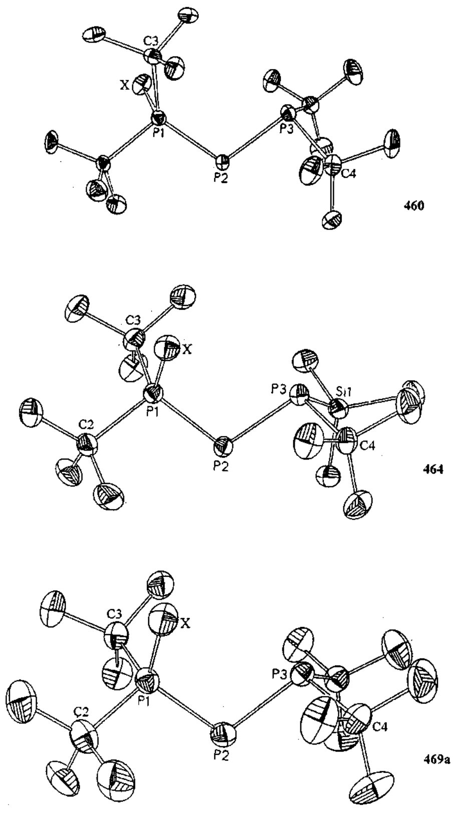


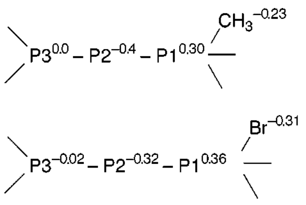
Figure 32. Molecular structures of the phosphinophosphinidene phosphoranes tBu$_2$P3−P2=P1(X)tBu$_2$ (X = Br (**460**), Me (**469a**)) and tBu(Me$_3$Si)$_2$P3−P2=P1(Me)tBu$_2$ (**464**). Reprinted with permission from refs 198 and 199. Copyright 1994 Wiley-VCH Verlag GmbH.

Table 20. ^{31}P NMR Data of the Phosphinophosphinidene Phosphoranes tBu$_2$P3−P2=P1(X)tBu$_2$ (X = Br (460), Me (469a)) and tBu(Me$_3$Si)$_2$P3−P2=P1(Me)tBu$_2$ (464)[a]

	^{31}P (ppm)			J (Hz)		
	P^1	P^2	P^3	$J_{(1,2)}$	$J_{(1,3)}$	$J_{(2,3)}$
460	172.27	−89.00	14.84	−681.6	−252.0	38.6
464	57.25	−212.88	−81.35	−603.8	−238.4	51.5
469a	57.49	−204.73	31.98	−596.7	−274.8	63.7

[a] In toluene-d_8/THF at −70 °C.

there is not yet a (full) 3pπ bond, as shown in the valence structure of **II**. The atomic charges of the P atoms[200] give further evidence for the mixing of structures **I** and **II** (calculated for R = tBu).



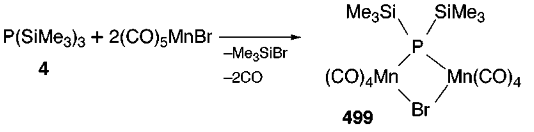
In the Br derivative the negative partial charge at P2 is slightly reduced as compared to the Me compound, indicating a larger delocalization of the lone pair and a stronger pπ bond. These results are in agreement with the P−P distances, showing a shorter P2−P1 bond in the Br compound than in the Me derivative. In comparison to P3, the larger positive charge at P1 causes a shorter P1−C bond (in comparison to P3−C) due to the contraction of the covalent radius of the P atom by electron withdrawing and the strengthening of the P1−C bond by Coulomb effects.

According to their SCF energies the triphosphanes were found to be somewhat more stable than the corresponding ylides; only the conformer tBu$_2$P−P=P(X)tBu$_2$ (X = Me (**469a**)) is an insignificant 3 kJ/mol more stable in the ylidic form. The relative stability of the ylides was found to increase in the sequence of the substituents X = H, Br, Cl, and Me.[199]

XI. Reactions of Transition Metal Halides with Silylphosphanes and LiP(SiMe$_3$)$_2$

Complexes with P(SiMe$_3$)$_2$- and P$_2$-bridges result from reactions of silylphosphanes with transition metal carbonyl halides. Metal clusters were synthesized when treating silylated compounds of group 15 and 16 elements with transition metal halides in the presence of phosphanes.

In the silylphosphane **4** only one Si−P bond was cleaved by the transition metal halide (CO)$_5$MnBr, forming the P-functionally bridged manganese carbonyl complex **499** (164). With methanol both Si−P bonds in **499** could be cleaved, resulting in the PH$_2$-bridged complex [Mn$_2$(CO)$_8$(μ-Br)(μ-PH$_2$)], the chlorination of which with CCl$_4$ results in [Mn$_2$(CO)$_8$(μ-Br)(μ-PCl$_2$)].[201]



(164)

From the corresponding reaction of Me$_3$Si−PH$_2$ (**59**) with (CO)$_5$MnCl the four-membered [(CO)$_4$Mn−PH$_2$]$_2$ and the six-membered [(CO)$_4$Mn−PH$_2$]$_3$ are accessible by elimination of Me$_3$SiCl and CO. Using CX$_4$ (X = Cl, Br, I), [(CO)$_4$Mn−PH$_2$]$_2$ can be halogenated yielding [(CO)$_4$Mn−PX$_2$]$_2$. Only in case of CCl$_4$ the halogenation of the six-membered ring leads to a completely P-halogenated [(CO)$_4$Mn−PCl$_2$]$_3$. A fluorination is observed when treating the compounds [(CO)$_4$Mn−PX$_2$]$_2$ (X = Cl, Br, I) and [(CO)$_4$Mn−PCl$_2$]$_3$ with Ag[BF$_4$] resulting in [(CO)$_4$Mn−PF$_2$]$_2$ and [(CO)$_4$Mn−PF$_2$]$_3$, respectively.[202] The reactions of the pentacarbonylmanganese halides (CO)$_5$MnX (X = Cl (**a**), Br (**b**), J (**c**)) with the silylphosphanes Ph$_{3-n}$P(SiMe$_3$)$_n$ (n = 1 (**3**), 2 (**177**), 3 (**4**)) at ambient temperature result in the elimination of one CO ligand and the formation of the substitution products X(CO)$_4$MnPPh$_{3-n}$(SiMe$_3$)$_n$ (n = 1 (**500a**−**c**), n = 2 (**501a**−**c**), n = 3 (**502a**−**c**)). The mononuclear complexes (**500**−**502**)**a**,**b** can be transformed into the binuclear derivative [(CO)$_4$MnPPh$_2$]$_2$ by thermal treatment. However, this transformation cannot be observed in the case of the iodine-substituted complexes (**500**−**502**)**c**. No CO substitution, but halogenosilane elimination, is observed, if the dicarbonylcyclopentadienyliron halides $Cp(CO)_2FeX$ (X = Cl, Br, I) react with $Ph_{3-n}P(SiMe_3)_n$ (n = 1 (**3**), 2 (**177**), 3 (**4**)) to give the di- and triferriophosphonium halides $[\{Cp(CO)_2Fe\}_2P(Ph)R]X$ (R = Ph, H) and $[\{Cp(CO)_2Fe\}_3PH]X$.[203]

The product range of mixed substituted diorganyldiferriophosphonium halides can be extended by functionalization of the used silylphoshane with R (R = Me, CH_2Ph).[204] The reaction of **4** with an excess of $Cp(CO)_2FeX$ (X = Cl, Br) through the action of water gives the P−H functional triferriophosphonium salts $[\{Cp(CO)_2Fe\}_3PH]_2FeX_4$ together with CO and ferrocene as byproducts. The cation of the salt $[\{Cp(CO)_2Fe\}_3PH]_2FeCl_4$ can be deprotonated by DBU (1,8 diazabicyclo[5.4.0]undec-7-ene) to afford the triferriophosphine $\{Cp(CO)_2Fe\}_3P$. Its subsequent realkylation with RX (R = Me, CH_2Ph; X = I, Br) leads to the alkyltriferriophosphonium salts $[\{Cp(CO)_2Fe\}_3PR]X$. Photolysis of $[\{Cp(CO)_2Fe\}_3PH]_2FeX_4$ induces the elimination of one CO group, and the CO-bridged complex $[\{\mu\text{-}CO(CpFeCO)_2\}\{CpFe(CO)_2PH]_2FeX_4$ with one Fe−Fe bond is formed. In the case of X = Cl the complex can be deprotonated with DBU to give the corresponding monobridged phosphine $[\{\mu\text{-}CO(CpFeCO)_2\}\{CpFe(CO)_2]P$. Both PH-phosphonium salts $[\{Cp(CO)_2Fe\}_3PH]_2FeCl_4$ and $[\{\mu\text{-}CO(CpFeCO)_2\}\{CpFe(CO)_2PH]_2FeCl_4$, respectively, undergo with CCl_4 a hydrogen−chlorine exchange, which results in the P−Cl analogous $[\{Cp(CO)_2Fe\}_3PCl]_2FeCl_4$ and $[\{\mu\text{-}CO(CpFeCO)_2\}\{CpFe(CO)_2PCl]_2FeCl_4$.[205]

From the reaction of $cp(CO)_2FeX$ (X = Cl (**a**), Br (**b**)) and $LiP(SiMe_3)_2$ (**80**) the iron complex $cp(CO)_2FeP(SiMe_3)_2$ (**503**), containing a terminal P-functional phosphido group, was obtained which with $Ni(CO)_4$ or $Fe_2(CO)_9$ generates the $P(SiMe_3)_2$-bridged $cp(CO)_2Fe[\mu\text{-}P(SiMe_3)_2]Ni(CO)_3$ (**504a**) or $cp(CO)_2Fe[\mu\text{-}P(SiMe_3)_2]Fe(CO)_4$ (**504b**), respectively. Using methanol the Si−P bonds of the bridging $P(SiMe_3)_2$ groups in both compounds can be cleaved to give the PH_2-bridged $cp(CO)_2Fe[\mu\text{-}PH_2]Ni(CO)_3$ (**505a**) and $cp(CO)_2Fe[\mu\text{-}PH_2]Fe(CO)_4$ (**505b**). Both complexes are also accessible by reacting $cp(CO)_2FeBr$ with $Me_3SiPH_2Ni(CO)_3$ (**506**) or $Me_3SiPH_2Fe(CO)_4$ (**507**), respectively. The derivatives **506** and **507** can also be synthesized from **59** and $Ni(CO)_4$ or $Fe_2(CO)_9$ according to (165, 166).[206]

$$Ni(CO)_4 + \underset{\mathbf{59}}{Me_3Si{-}PH_2} \rightarrow \underset{\mathbf{506}}{(CO)_3NiPH_2SiMe_3} + CO \quad (165)$$

$$Fe_2(CO)_9 + \underset{\mathbf{59}}{Me_3Si{-}PH_2} \rightarrow \underset{\mathbf{507}}{(CO)_4FePH_2SiMe_3} + Fe(CO)_5 \quad (166)$$

The iron complex $cp(CO)_2Fe[\mu\text{-}PH_2]Fe(CO)_4$ (**505b**) was established by a single crystal X-ray analysis.[207]

Compound **503** reacts with the carbonyl nitrosyl complexes $Co(CO)_3(NO)$, $Fe(CO)_2(NO)_2$, and $Mn(CO)(NO)_3$ by substituting a CO ligand (167) and with $M'L_mTHF$ (168) by substituting the THF ligand to give the phosphido-bridged dinuclear complexes **504c**−**j**.[208]

$$\underset{\mathbf{503}}{Cp(CO)_2FeP(SiMe_3)_2} + \underset{\substack{M' = Mn,\ x = 1\\ = Fe,\ x = 2\\ = Co,\ x = 3}}{M'(CO)_x(NO)_{4-x}} \xrightarrow[-CO]{} \underset{\substack{\mathbf{504c}\\ \mathbf{504d}\\ \mathbf{504e}}}{cp(CO)_2Fe[\mu\text{-}P(SiMe_3)_2]M'(CO)_{x-1}(NO)_{4-x}} \quad (167)$$

$$\mathbf{503} + M'L_mTHF \rightarrow cp(CO)_2Fe[\mu\text{-}P(SiMe_3)_2]M'L_m + THF \quad (168)$$

$$\begin{array}{ll} M'L_m = Cr(CO)_5 & \mathbf{504f} \\ Mo(CO)_5 & \mathbf{504g} \\ W(CO)_5 & \mathbf{504h} \\ Mncp(CO)_2 & \mathbf{504i} \\ MnMecp(CO)_2 & \mathbf{504j} \end{array}$$

Cleaving both Si−P bonds in **504c**−**k** ($M'L_m$ = Crcp(CO)(NO) (**k**)) by using either CH_3OH, H_2O, or CH_3COOH gives the PH_2-bridged dinuclear complexes **505c**−**k**.[209]

nBuLi selectively cleaves a Si−P or H−P bond in $L_mM'P(SiMe_3)_3$ (**508b**,**f**−**l**) and $L_mM'PH_3$ (**509b**,**f**,**j**) (169). The lithiated compounds **510b**,**k**,**l** and **511b**,**f**,**j** react with $cp(CO)_2FeBr$ to give the dinuclear **504b**,**f**−**l** and **505b**,**f**,**j** again (170). The used complexes $L_mM'PH_3$ (**509b**,**f**,**j**) are accessible by methanolysis of $L_mM'P(SiMe_3)_3$ (**508b**,**f**,**j**).

$$L_mM'P(R)_3 + n\text{BuLi} \rightarrow \underset{\substack{\mathbf{510b,f{-}l}\\ \mathbf{511b,f,j}}}{L_mM'P(R)_2Li} + RBu \quad (169)$$

$$\begin{array}{ll} R = SiMe_3 & \mathbf{508b,f{-}l} \\ R = H & \mathbf{509b,f,j} \\ M'L_m = & Fe(CO)_4\ (\mathbf{b}) \\ & Cr(CO)_5\ (\mathbf{f}) \\ & Mo(CO)_5\ (\mathbf{g}) \\ & W(CO)_5\ (\mathbf{h}) \\ & Mncp(CO)_2\ (\mathbf{i}) \\ & MnMecp(CO)_2\ (\mathbf{j}) \\ & Crcp(CO)(NO)\ (\mathbf{k}) \\ & Vcp(CO)_3\ (\mathbf{l}) \end{array}$$

$$\mathbf{510b,f{-}l/511b,f,j} + cp(CO)_2FeBr \rightarrow cp(CO)_2Fe[\mu\text{-}P(R)_2]M'L_m + LiBr \quad (170)$$

$$\begin{array}{ll} R = SiMe_3 & \mathbf{504b,f{-}l} \\ R = H & \mathbf{505b,f,j} \end{array}$$

The open chain complexes **504** and **505** undergo a photochemical decarbonylation to form the phosphido-bridged dinuclear complexes $cp(CO)Fe[\mu\text{-}CO,\mu\text{-}P(R)_2]M'L_{m-1}(Fe{-}M')$ (R = $SiMe_3$ (**512**), H (**513**)) containing a metal−metal bond (171).[208,209]

$$\begin{array}{ll} \mathrm{cp(CO)_2Fe[\mu\text{-}P(R)_2]M'L}_m & \\ \mathrm{R = SiMe_3} \quad \mathbf{504d,f,h{-}k} & \\ \mathrm{R = H} \quad \mathbf{505i,j} & \downarrow \\ \mathrm{cp(CO)Fe[\mu\text{-}CO,\mu\text{-}P(R)_2]M'L}_{m-1}\mathrm{(Fe{-}M') + CO} & \\ \quad \mathbf{512d,f,h{-}k} & \\ \quad \mathbf{513i,j} & \\ \mathrm{M'L}_{m-1} = \mathrm{Fe(NO)_2}\ (\mathbf{d}) & \\ \qquad \mathrm{Cr(CO)_4}\ (\mathbf{f}) & \\ \qquad \mathrm{W(CO)_4}\ (\mathbf{h}) & \\ \qquad \mathrm{Mncp(CO)}\ (\mathbf{i}) & \\ \qquad \mathrm{MnMecp(CO)}\ (\mathbf{j}) & \\ \qquad \mathrm{Crcp(NO)}\ (\mathbf{k}) & (171) \end{array}$$

LiP(SiMe$_3$)$_2$ (**80**) and cp(PPh$_3$)NiCl react by LiCl elimination to give the nickel complex cp(PPh$_3$)NiP(SiMe$_3$)$_2$ (**514**) containing a terminal phosphido group. With Ni(CO)$_4$ the Ni−P four-membered ring [cpNiP(SiMe$_3$)$_2$]$_2$ (**515**) results via a complex reaction series with intermediates, in which the PPh$_3$ ligand has been substituted by CO. Cleaving the Si−P bonds in **515** with methanol, a ring expansion is observed, forming the six-membered [cpNiPH$_2$]$_3$, which can also be obtained directly by reacting cp(PPh$_3$)NiCl with **59**.[210]

Reactions of the dichloro complexes (R$_3$P)$_2$MCl$_2$ of platinum and nickel with **80** (Scheme 35) in a molar ratio of 1:2 at low temperatures result via the mono- or disubstituted intermediates (R$_3$P)$_2$M[P(SiMe$_3$)$_2$]Cl (**516**, **517**) and (Et$_3$P)$_2$Pt[P(SiMe$_3$)$_2$]$_2$ (**518**) in the diphosphene complexes (R$_3$P)$_2$M′[η^2-(Me$_3$SiP=PSiMe$_3$)] (**520** and **521**) as well as in the phosphido-bridged metal(I) complexes (R$_3$P)M′[μ-P(SiMe$_3$)$_2$]$_2$M′(PR$_3$) (**522** and **523**). In this case the choice of the substituents R as well as the temperature has an important influence on the resulting products. No disubstituted nickel complex, the analogue to **518**, could be detected. Instead, a parallel redox reaction to the nickel(0) diphosphane complexes **519** was observed, partly even favored as compared to the formation of the diphosphene complex. For the formation of the complexes **523** with a Ni−Ni bond a radical mechanism was proposed. Heating of the monosubstitution products **516** and **517** gives the P$_2$ complexes **524** and **525**. Compounds **520** and **524** can also be obtained by reacting (Et$_3$P)$_2$PtCl$_2$ with (Me$_3$Si)$_2$P−P(SiMe$_3$)$_2$ (**185**). The asymmetric analogous of **520**, the diphosphene complex (Et$_3$P)$_2$Pt[η^2-(Me$_3$SiP=P*t*Bu)] (**520a**) results from (Et$_3$P)$_2$PtCl$_2$ and (Me$_3$Si$_2$)P−P(*t*Bu)SiMe$_3$ (**191**). This procedure using silylated diphosphanes also turned out to be the most favorable synthesis for nickel diphosphene complexes. All compounds were characterized by ^{31}P NMR analysis.[211−213] Additionally, a nearly coplanar coordination of the Ni center was found in a single crystal X-ray determination of **521b**. The bond length P2−P3 with 214.8 ppm is significantly shorter than a normal P−P single bond (Figure 33).[214]

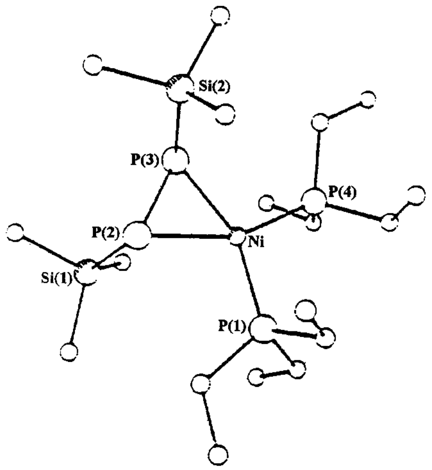
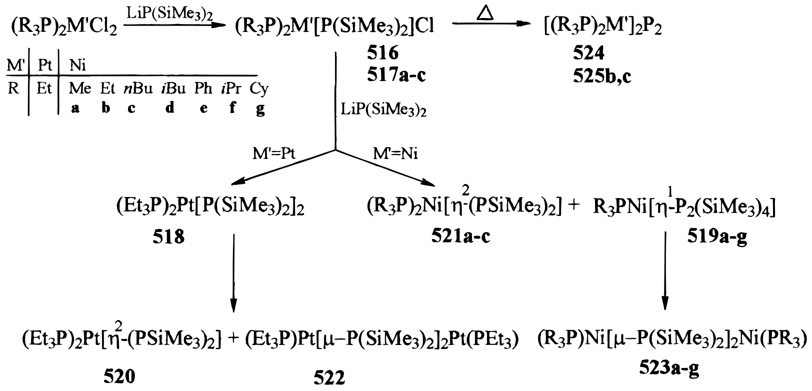


Figure 33. Molecular structure of (Et$_3$P)$_2$Ni[η^2-(Me$_3$SiP=PSiMe$_3$)] (**521b**). Reprinted with permission from ref 214. Copyright 1982 International Union of Crystallography.

In an analogous way the chelat compounds (DRPE)NiCl$_2$ (DRPE = R$_2$PCH$_2$CH$_2$PR$_2$; R = Et (**a**), Cy (**b**), Ph (**c**)) react with **80** via the intermediates (DRPE)Ni[P(SiMe$_3$)$_2$]Cl (**526a**−**c**) and (DRPE)Ni[(P(SiMe$_3$)$_2$]$_2$ (**527a**,**c**) to form the diphosphene complexes (DRPE)Ni[η^2-(PSiMe$_3$)$_2$] (**528a**−**c**). In the case of R = Cy the nickel(I) complex (Cy$_2$PCH$_2$CH$_2$PCy$_2$)NiP(SiMe$_3$)$_2$ (**529**) could be isolated and characterized by an X-ray investigation, which showed the nickel(I) to be nearly planar coordinated by three P atoms.[215,216] From reactions with the silylphosphanes P(SiMe$_3$)$_3$ (**4**), HP(SiMe$_3$)$_2$ (**87**), Me$_3$Si−PH$_2$ (**59**), and (Me$_3$Si)$_2$P−P(SiMe$_3$)$_2$ (**185**) result the diphosphorus complexes [(DRPE)Ni]$_2$P$_2$ (**530a**−**c**) and the nickel(0) complexes (DRPE)$_2$Ni (**531a**−**c**). The diphosphene complex (DRPE)$_2$Ni[η^2-(HP=PH)] (**532b**), accessible by treating the starting nickel compound (R = Cy) with **59**, could be isolated at low temperature. Cleaving the Si−P bonds in the diphosphene complexes **528a**,**b**

Scheme 35

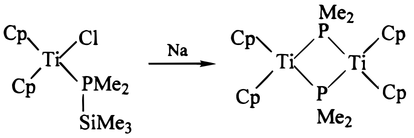


with methanol gives the P_2 complexes **530a**,**b**. Products containing asymmetric diphosphene ligands can be obtained by reaction with $(Me_3Si)P{-}P(tBu)SiMe_3$ (**175**), the methanolysis of which also yields the P_2 complexes **530a**,**b**.[217]

$(\eta^5\text{-}C_5H_5)_2TiCl_2$ reacts with **45** to form the paramagnetic green complex **533** (172). Even at higher temperature no further chlorine substitution could be observed.

$$\underset{}{Cp_2TiCl_2} + \underset{\mathbf{45}}{2Me_3Si{-}PMe_2} \rightarrow \underset{\mathbf{533}}{Cp_2Ti[PMe_2(SiMe_3)]Cl} + Me_3SiCl \quad (172)$$

Treatment of **533** with sodium amalgam affords under elimination of Me_3SiCl the binuclear paramagnetic complex **534** (173).[218]



533 **534** (173)

The synthesis of the tetranuclear copper(I) silylphosphido cluster $[Cu(CyPSiMe_2PHCy)]_4$ (**535**) (Figure 34) was possible by reacting the silylphosphanes $Me_2Si(NEt_2)PHCy$ (**536**) or $Me_2Si(PHCy)_2$ (**537**), respectively, with the benzene solvate of copper(I) trifluoromethylsulfonate. The Cu_4-tetrahedron in **535** is chelate-like, surrounded by four $[CyPH{-}SiMe_2{-}CyP]^-$ ligands.[219]

A large number of metal-rich cluster compounds have been synthesized in reactions of phosphane complexes of transition metal halides with silyl derivatives of group 15 and 16 compounds.[220] The driving force of these reactions is the elimination of Me_3SiCl, and the cluster formation is facilitated by the shielding effect of the phosphane ligands. The steric demands of the phosphane ligands also influence the size and structure of the cluster.[221]

The following short summary just points out the importance of this research area. A comprehensive presentation including all structures of clusters should have to be given separately. The reaction of $CoCl_2{\cdot}2PPh_3$ with $PhP(SiMe_3)_2$ (**177**) offers a simple entry to the tetranuclear cluster $[Co_4(\mu_3\text{-}PPh)_4(PPh_3)_4]$ (**538**) (Figure 35). Each surface of this tetrahedral Co_4-cluster is coordinated by a μ_3-PPh ligand, and each Co atom is bond to a PPh_3 ligand.

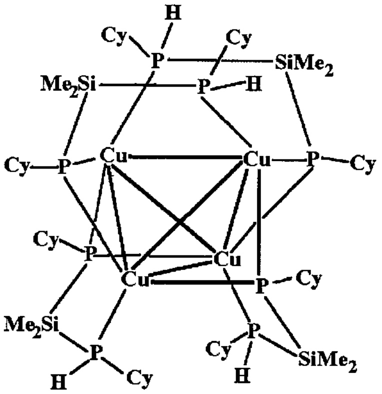


Figure 34. Molecular structure of the chelated cluster $[Cu(CyPSiMe_2PHCy)]_4$ (**535**). Reprinted with permission from ref 219. Copyright 1998 Royal Society of Chemistry.

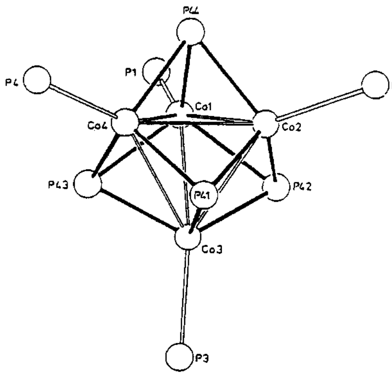


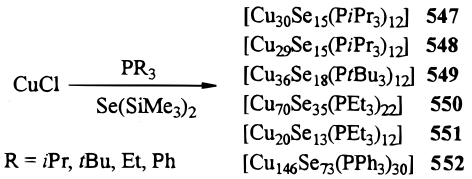
Figure 35. Molecular structure of $[Co_4(\mu_3{-}PPh)_4(PPh_3)_4]$ (**538**) (the phenyl groups are not shown for sake of clarity). P1, P2, P3, and P4 signify the P atoms of the PPh_3 ligands; P41, P42, P43, and P44, the P atoms of the μ_3-PPh ligands. Reprinted with permission from ref 222. Copyright 1984 Wiley-VCH Verlag GmbH.

In the analogous reaction of $NiCl_2$ with PPh_3 and **177** the silylphosphane is not completely consumed. Addition of acetyl chloride leads to the clusters $[Ni_8Cl_4(PPh)_6(PPh_3)_4]$ (**539a**) and $[Ni_8(CO)_4(PPh)_6(PPh_3)_4]$ (**539b**), which can be isolated by fractional crystallization.[220a,222]

That syntheses of clusters are also possible without terminal phosphane ligands and could be demonstrated by the reaction of $NiCl_2$ with **177** in THF solution, forming black crystals of the Ni_{12}-cluster $[Ni_{12}Cl_2(\mu_4\text{-}PPh)_2(\mu_6\text{-}P_2Ph_2)_4(PHPh)_8]$ (**540**). The PHPh ligands result from the reaction of the silylphosphane with traces of H_2O.[223]

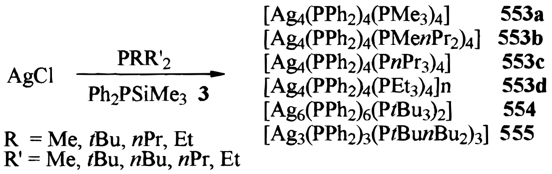
Already in 1968 the synthesis of insoluble oligomeric products such as $[CuPPh_2]_n$ in reactions of CuCl with Ph_2PSiMe_3 (**3**) by elimination of Me_3SiCl was reported.[224] In analogous investigations in the presence of tertiary phosphanes $RPPh_2$ ($R = n$Pr, H) or PMe_3, respectively, multinuclear copper clusters, e.g. $[Cu_4Cl(PPh_2)_3(nPrPPh_2)_3]$ (**541**), could be isolated and structurally elucidated. A completely different structure is obtained if the sterically less demanding PMe_2 bridging ligands are used instead of PPh_2. The formed $[Cu(PMe_3)_4]_2[Cu_{13}Cl_6(PMe_2)_9]$ (**542**) from the reaction of CuCl with **45** and PMe_3 consists of two $[Cu(PMe_3)_4]^+$ and one $[Cu_{13}Cl_6(PMe_2)_9]^{2-}$. The controlling influence of the bridging ligands on the structure of the Cu cluster is also obvious in the reaction of CuCl with $PHPh_2$ and a mixture of **3** and **177**, resulting in $[Cu_{18}(PPh)_4(PPh_2)_{10}(PHPh_2)_3]$ (**543**). The reactions of CuCl with PR_3 (R = Me, Ph) and **177** show the effect of the tertiary phosphanes and of the silylphosphanes on the structures of the resulting clusters. With PPh_3, the cluster $[Cu_{12}(PPh)_6(PPh_3)_6]$ (**544**) and, with PMe_3, $[Cu_{14}(PPh)_6Cl_2(PMe_3)_8]$ (**545**) are formed.[225] With $P(SiMe_3)_3$ (**4**) the even higher bridged copper cluster $[Cu_{96}P_{30}\{P(SiMe_3)_2\}_6(PEt_3)_{18}]$ (**546**) is obtained, if the components CuCl, PEt_3, and **4** are used in the ratio of 1:0.5:0.6.[226] Also silyl derivatives of arsenic, sulfur, selenium, and tellurium compounds react with metal halides and tertiary phosphanes to give clusters, and again the structure of the formed cluster will depend on the phosphane ligand and its sterical demand.[220b,227] The products of the reaction between CuCl, $Se(SiMe_3)_2$, and different phosphanes PR_3 (R = *i*Pr, *t*Bu, Et, Ph) are summarized in Scheme 36. The clusters **547** and **549** have diamagnetic and **548** has paramagnetic properties.[228−230]

Scheme 36



To which extent the synthetic concept of the copper clusters is transferable to the elements silver, zinc, and cadmium was investigated by the corresponding reactions of transition metal salts with silylphosphanes in the presence of stabilizing phosphane ligands. AgCl reacts with Ph_2PSiMe_3 (**3**) and PRR'_2 to form the multinuclear Ag complexes in Scheme 37, which were characterized by single-crystal X-ray structure analyses.[231,232]

Scheme 37



The analogous reactions of zinc and cadmium salts MCl_2 with **3** and tertiary phosphanes PRR'_2 (R = *n*Pr, R′ = *n*Pr (**a**); R = *n*Bu, R′ = *n*Bu (**b**); R = Me, R′ = *n*Pr (**c**); R = Ph, R′ = Et (**d**)) in THF solution lead to the multinuclear complexes $[M_4Cl_4(PPh_2)_4(PRR'_2)_2]$ (M = Cd (**556a**); M = Zn (**557a**−**d**). Compounds **556a** and **557a** form adamantane structures consisting of the four metal atoms with four μ_2−PPh_2 and two μ_2−Cl groups as well as two *n*Pr and two Cl ligands.[230,231] However the compounds $[Zn_4(PhPSiMe_3)_4Cl_4(C_4H_8O)_2]$ and $[Zn_4(PtBu_2)_4Cl_4]$ were obtained by reacting $ZnCl_2$ with **177** or tBu_2PSiMe_3 (**558**), respectively, without tertiary phosphanes.[232]

In the reactions of ZnI_2 or CdI_2 with the higher silylated **4** in diethyl ether or DME, respectively, no elimination of Me_3SiI could be observed, but a coordination of **4** to form the binuclear complex $[MI_2\{P(SiMe_3)_3\}]_2$ (M = Zn (**559**), Cd (**560**)). Further reactions of **559** and **560** with $NnBu_4I$ result in the ionic compounds $[NnBu_4]_2[Zn_6I_6(PSiMe_3)_4(C_4H_8O)_2]\cdot C_6H_6$ (**561**) and $[NnBu_4]_2[Cd_4I_8\{P(SiMe_3)_2\}_2]$ (**562**), respectively, by elimination of Me_3SiI. In the presence of the tertiary phosphane PEt_2Ph in case of $ZnCl_2$, $[Zn_{10}Cl_{12}(PSiMe_3)_4(PEt_2Ph)_4]$ (**563**) is formed, or in the case of CdI_2 the ionic Cd_{18} complex $[PhEt_2PC_4H_8OSiMe_3]_5[Cd_{18}I_{17}(PSiMe_3)_{12}]$ (**564**).[233,234]

Whereas reactions of the metal halides AgCl or $ZnCl_2$ with **3** do not yield metal-rich clusters, reactions of AgCl with the higher silylated phosphane $PhP(SiMe_3)_2$ (**177**) in the presence of PR_3 (R_3 = Me_3, $MeEt_2$, $MenPr_2$, Et_3, nPr_3) provides access to phosphinidene-bridged silver clusters. In the case of $PnPr_3$ the clusters $[Ag_{18}(PPh)_8(PhPSiMe_3)_2(PnPr_3)_8]$ (**565**), $[Ag_{45}(PPh)_{18}(PhPSiMe_3)_2Cl_7(PnPr_3)_{12}]$ (**566**), and $[Ag_{50}(PPh)_{20}Cl_7P(PnPr_3)_{13}]$ (**567**) were characterized by X-ray structure analysis. The Ag_{18} polyhedron **565** (Figure 36) consists of two trigonal prisms of silver atoms connected to each other through a common surface. Two cubes are condensed onto the surfaces formed by Ag1−Ag4 and Ag1′−Ag4′, respectively. One of the cube faces in each case is bridged by a silver atom, which at the same time caps the prism edge (Ag3, Ag4 and Ag3′, Ag4′, respectively). The P atoms of the bridging ligands (PPh and $PhPSiMe_3$) function as μ_2-(P5), μ_3-(P4), μ_4-(P1,P3), and μ_5-(P2) bridges. The terminal-bound $PnPr_3$ ligands (P6−P9) are all coordinated to silver atoms at the surface of the cube that is capped by Ag6. The compound still contains a reactive $SiMe_3$ group coordinated to P5, which could conceivably lead to further cluster formation. Inside clusters **566** and **567** is formed a silver atom framework on which surface the PPh, $PhPSiMe_3$, $PnPr_3$, and Cl ligands are coordinated.[221]

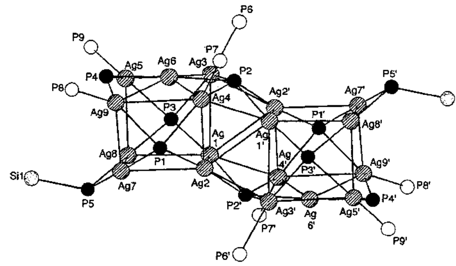
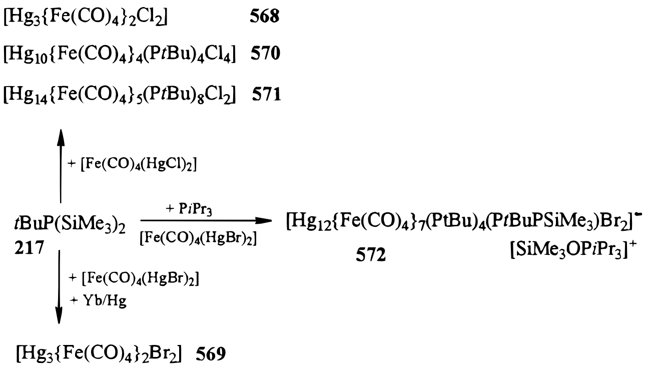


Figure 36. Molecular structure of $[Ag_{18}(PPh)_8(PhPSiMe_3)_2(PnPr_3)_8]$ (**565**). Reprinted with permission from ref 221. Copyright 1997 Wiley-VCH Verlag GmbH.

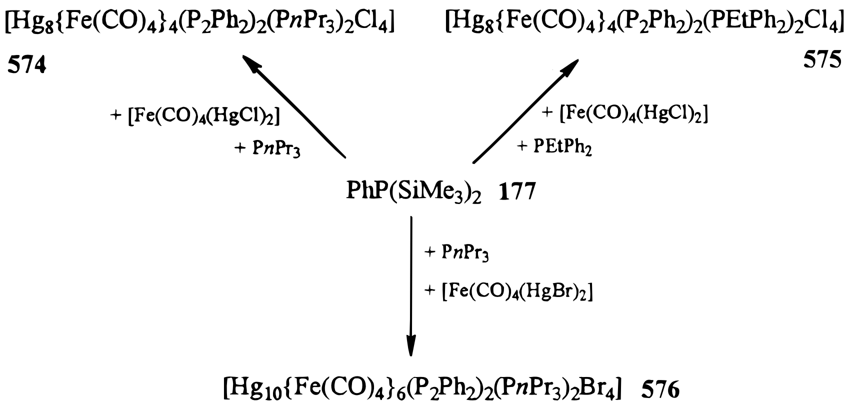
Depending on the molar ratio of the educts, the reaction of $[Fe(CO)_4(HgX)_2]$ (X = Cl, Br) with $tBuP(SiMe_3)_2$ (**217**) leads to the multinuclear complexes **568** and **569** as well as to the phosphinidene-bridged mercury clusters **570** and **571** (Scheme 38). In the presence of $PiPr_3$ the ionic cluster **572** and, when using tBu_2PSiMe_3 (**558**), the phosphanido-bridged cluster $[Hg_5\{Fe(CO)_4\}(PtBu_2)_2Br_2]$ **573** results.

Scheme 38



The reaction of $[Fe(CO)_4(HgX)_2]$ (X = Cl, Br) with **177** and PR_3 (R_3 = nPr, $EtPh_2$) yields the phosphanido-bridged clusters **574**−**576** (Scheme 39). The structures of **568**−**576** were characterized by single crystal X-ray structure analysis.[235]

Scheme 39



Although monometallic diorganophosphanes MPR_2 ($R =$ alkyl, aryl, silyl) have been widely investigated, not very much is known about the reactivity and structures of phosphanes with two metal atoms attached to the phosphorus (phosphanediyl complexes) M_2PR. Dilithium derivatives of primary amines, phosphanes, and arsanes of the type $[RELi_2]_n$ ($R =$ alkyl, aryl, silyl; $E =$ N, P, As) are useful nucleophilic building blocks in the element organic chemistry of nitrogen, phosphorus, and arsenic. They are molecular aggregates, which structurally represent an intermediate between the molecular compounds R_3E and the salt-like solid-state compounds Li_3P. [25,48a,73,110,236]

Structurally characterized are the decameric dilithium (α-naphthyl)azanediide $[(RNLi_2)_{10}(Et_2O)_6]\cdot Et_2O$ ($R = \alpha\text{-}C_{10}H_7$)[237] and the dimeric dilithium phosphanediide–fluorosilane adduct $RPLi_2\cdot 2\ RF$ ($R = Si\mathit{i}Pr_2(2,4,6\text{-}\mathit{i}Pr_3C_6H_2)$).[238] The double lithiation of the silylphosphane RPH_2 ($R = Si\mathit{i}Pr_2(2,4,6\text{-}Me_3C_6H_2)$) with *n*BuLi in the presence of Li_2O results in the octameric $[(RP)_8Li_{18}O]$. The corresponded reaction with the silylarsane $RAsH_2$ ($R = Me_2(\mathit{i}PrMe_2C)Si$) leads to the dodecameric $[(RAs)_{12}Li_{26}O]$. The cavities of both compounds are filled with an octahedral $[Li_6O]^{4+}$ cluster framework. The $[(RP)_8Li_{18}O]$ cluster has eight formula units of dilithium phosphanediide and a Li_2O molecule. The cationic (Li centers) and anionic (P and O centers) building blocks show close packing. The topological best description of this structure is an ionogenic cluster formed by three closed shells and covered by the lipophilic silyl groups. The eight P atoms comprise a strongly distorted cube, which is surrounded by a Li_{12} cuboctahedral shell and surrounds a Li_6O octahedron. The three shells cluster $[(RAs)_{12}Li_{26}O]$ is topologically closely related to the phosphorus cluster.[239] A neutral copper phosphanediyl cluster $[(RP)_{12}Cu_{24}]$ was prepared in the reaction of RPH_2 ($R = SiMe_2(\mathit{i}PrMe_2C)$) with $[\{CuO\mathit{t}Bu\}_4]$ in toluene as dark red crystals. The structure shows a cluster of 24 Cu atoms surrounded by 12 triorganosilylphosphanediyl groups. The 24 atom cluster consists of three planar Cu_6 rings and two peripheral Cu_3 rings that all lie parallel to one other. The twelve PR fragments cap alternately the Cu_4 faces of the Cu_{24} polyhedron resulted in 5-fold-coordinated P centers.[240]

XII. Reactions of Halogenated Compounds of Group 13 Elements with Silylated Compounds of Group 15 Elements of the Periodic Table

Many investigations have centered on the formation of potential groups 13–15 semiconductors, which lead either to the addition products $R_3E^{13}\cdot E^{15}R'_3$ or to cycles with an $E^{13}-E^{15}$ molecular skeleton, in which four-membered rings are preferred. The results of these investigations have been reviewed in different papers.[241,242] In Table 21 the published results are summarized.[243–279]

XIII. Reactions of Silylphosphanes with Sulfur and CS_2

The liability of silylphosphanes against oxygen leads in the case of **4** or $Me_3Si-PPh_2$ (**3**), respectively, to $(Me_3SiO)_3P(O)$[280] or $Me_3SiOP(O)$[281] by simultaneously proceeding insertion and oxidation. Also insertions into the Si–P bond in reactions with CO_2, CS_2, and SO_2 are described.[280] With elemental sulfur silylphosphanes react in the same way; e.g. **3** forms $Me_3Si(S)P(S)PPh_2$.[282] Further examples for reactions of silylphosphanes with S_8 and their products are summarized in Table 22, which shows that the reaction capability decreases from **45** to **185**. In pentane or hexane, these reactions run much slower. So, depending on the molar ratio, isolable intermediates are formed.

The unstable compound **585** decomposes during some hours (174).

$$\underset{\mathbf{585}}{2Me_3Si(S)PMe_2} \rightarrow Me_2P(S)PMe_2 + (Me_3Si)_2S \tag{174}$$

Also pure **579**, which could be obtained by a HPLC separation, decomposes according to (175).

$$\underset{\mathbf{579}}{5(Me_3SiS)(SiMe_3)PMe} \rightarrow (PMe)_5 + 5(Me_3Si)_2S \tag{175}$$

In the reactions of the diphosphane **185** with elemental sulfur in hexane solution, insertion and cleavage of the P–P as well as of the Si–P bond occur simultaneously, depending on the molar ratio of the components. The resulting products using a ratio of

Table 21. Reactions between Halogenated Element 13 Compounds with Silylated Element 15 Compounds

	products	analysis	ref
BX_3 (X = Cl, Br, I)			
+ $P(SiMe_3)_3$, 1:1	$X_3B{\cdot}P(SiMe_3)_3$	X-ray	243
+ $LiP(SiMe_3)_2$, 1:1	$[X_2BP(SiMe_3)_2]_2$	X-ray	243
AlX_3 (X = Cl, Br) + $P(SiMe_3)_3$, 1:1	$X_3Al{\cdot}P(SiMe_3)_3$	X-ray	244
$2Et_2AlCl$			
+ 2 $LiP(SiMe_3)_2$	$[Et_2AlP(SiMe_3)_2]_2$	X-ray	245
+ $P(SiMe_3)_3$	$Et(Cl)_2Al{\cdot}P(SiMe_3)_3$, Et_3Al	X-ray	245
$2iBu_2AlCl$ + $P(SiMe_3)_3$	$iBu_2(Cl)Al{\cdot}P(SiMe_3)_3$, iBu_2AlCl	X-ray	245
$PhAlCl_2$ + $P(SiMe_3)_3$	$Ph(Cl)_2Al{\cdot}P(SiMe_3)_3$	NMR	246
Ph_2AlCl + $E(SiMe_3)_3$ (E = P, As), 1:1	$Ph_2AlCl{\cdot}E(SiMe_3)_3$ (E = P, As)	NMR, X-ray (E = As)	246
Ph_3Al + $E(SiMe_3)_3$ (E = P, As), 1:1	$Ph_3Al{\cdot}E(SiMe_3)_3$ (E = P, As)	NMR, X-ray	246
$(Me_3CCH_2)_3Al$ + $E(SiMe_3)_3$ (E = P, As), 1:1	$(Me_3CCH_2)_3Al{\cdot}E(SiMe_3)_3$	X-ray	247
$(Me_3SiCH_2)_3Al$ + $E(SiMe_3)_3$ (E = P, As) 1:1	$(Me_3SiCH_2)_3Al{\cdot}E(SiMe_3)_3$	X-ray (E = As)	247
$(Me_3SiCH_2)_2AlBr$			
+ $P(SiMe_3)_3$ 1:1	$(Me_3SiCH_2)_2BrAl{\cdot}P(SiMe_3)_3$	NMR, X-ray	247
+ $LiE(SiMe_3)_2$ (E = P, As)	$[(Me_3SiCH_2)_2AlE(SiMe_3)_2]_2$	NMR, X-ray (E = As)	247
$(Me_3SiCH_2)AlBr_2$ + $LiE(SiMe_3)_2$ (E = P, As)	$[(Me_3SiCH_2)_2BrAlE(SiMe_3)_2]_2$	NMR, X-ray	247
$AlH_3{\cdot}NMe_3$			
+ $P(SiMe_3)_3$	$[H_2AlP(SiMe_3)_2]_3$, AlP (950 °C)	XRD, X-ray	248
+ $As(SiMe_3)_3$	$[H_2AlAs(SiMe_3)_2]{\cdot}NMe_3$, AlAs (450 °C)	XRD, X-ray	248
Me_3Al			
+ $P(SiMe_3)_3$	$Me_3Al{\cdot}P(SiMe_3)_3$	NMR	249
+ $HP(SiMe_3)_2$	$[Me_2AlP(SiMe_3)_2]_2$	NMR	249
Me_2AlH			
+ $P(SiMe_3)_3$	$[Me_2AlP(SiMe_3)_2]_2$	NMR	249
+ $HP(SiMe_3)_2$	$[Me_2AlP(H)SiMe_3]_2{\cdot}Me_2AlP(SiMe_3)_2$	NMR, MS	250
GaX_3 (X = Cl, Br, I)			
+ $P(SiMe_3)_3$, 1:1	$GaX_3{\cdot}P(SiMe_3)_3 \rightarrow$ GaP (450 °C)	NMR, MS, X-ray, TGA	251, 252
+ $As(SiMe_3)_3$	GaAs, 3 Me_3SiCl		253
$GaCl_3$ + $P(SiMe_3)_3$, 2:1	$(Cl_3Ga_2P)_n \xrightarrow{300\ °C} Ga$	X-ray	251
$GaCl_3$ + $P(SiMe_3)_3$ + $As(SiMe_3)_3$	$(1/n)[\{Ga_2(As,P)\}Cl_3]_n \rightarrow GaAs_xP_y$	XRD	254
GaI_3 + $P(SiMe_3)_3$ + $As(SiMe_3)_3$, 2:1:1	$I_2GaAs(SiMe_3)_2Ga(I)_2P(SiMe_3)_2$	X-ray	255
$[I_2GaAs(SiMe_3)_2]_2$ + $[I_2GaP(SiMe_3)_2]_2$, 1:1	$I_2GaAs(SiMe_3)_2Ga(I)_2P(SiMe_3)_2$	X-ray	255
Me_2GaCl + $P(SiMe_3)_3$	$[Me_2GaP(SiMe_3)_2]_2$	X-ray	256
Ph_2GaCl			
+ $P(SiMe_3)_3$, 1:1	$Ph_2(Cl)Ga{\cdot}P(SiMe_3)_3$	X-ray	257
+ $P(SiMe_3)_3$, 2:1	$Ph_2GaP(SiMe_3)_2Ga(Ph)_2Cl$	NMR, X-ray	257
Bu_2GaCl + $P(SiMe_3)_3$, 1:1	$[Bu_2GaP(SiMe_3)_2]_2 \rightarrow$ GaP (400 °C)	X-ray	258
$BuGaCl_2$ + $P(SiMe_3)_3$	$[Bu(Cl)GaP(SiMe_3)_2]_2$		258
$(Me_3CCH_2)_2GaCl$ + $P(SiMe_3)_3$, 1:1	$(Me_3CCH_2)_2(Cl)Ga{\cdot}P(SiMe_3)_3$	X-ray	259
$(Me_3CCH_2)_2GaCl$ + $P(SiMe_3)_3$, 2:1	$[(Me_3CCH_2)_2(Cl)GaP(SiMe_3)_2]_2$	X-ray	259
$(Me_3SiCH_2)_2GaCl$ + $P(SiMe_3)_3$, 2:1	$(Me_3SiCH_2)_2GaP(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl$ (**A**)	X-ray	259
$(Me_3SiCH_2)_2GaBr$ + $P(SiMe_3)_3$, 2:1	$[(Me_3SiCH_2)_2(Br)GaP(SiMe_3)_2]_2$	X-ray	259
$(Me_3CCH_2)_2GaCl$ + $LiP(SiMe_3)_2$	$[(Me_3CCH_2)_2GaP(SiMe_3)_2]_2$ (**B**)	X-ray	259
A + $LiP(SiMe_3)_2$	$[(Me_3SiCH_2)_2GaP(SiMe_3)_2]_2$	NMR, X-ray	260
B + $(Me_3CCH_2)_2GaCl$, 1:2	$(Me_3CCH_2)_2GaP(SiMe_3)_2Ga(CH_2CMe_3)_2Cl$	X-ray	258
Ph_3Ga + $P(SiMe_3)_3$, 1:1	$Ph_3Ga{\cdot}P(SiMe_3)_3$	NMR, X-ray	261
Me_3Ga + $P(SiMe_3)_3$, 1:1	$[Me_2GaP(SiMe_3)_2]_2$	X-ray, TGA-DTA	249
Me_3Ga + $HP(SiMe_3)_2$	$[Me_2GaP(SiMe_3)_2]_2$	NMR	249
Me_3Ga + PMe_3	$Me_3Ga{\cdot}PMe_3$		262
$Me_3Ga{\cdot}PMe_3$ + $P(SiMe_3)_3$	$[Me_3Si)_2P\{Me_2Ga\}_2PMe]_2$		263
$(Me_3SiCH_2)_3Ga$ + $E(SiMe_3)_3$ (E = P, As)	$(Me_3SiCH_2)_3Ga{\cdot}E(SiMe_3)_3$		263
H_3Ga + $E(SiMe_3)_3$ (E = P, As)	$[H_2GaE(SiMe_3)_2]_3 \rightarrow$ nanocryst. GaP, AsP	NMR, MS, X-ray, XRD	264
$BiCl_3$ + $P(SiMe_3)_3$	BiP; 3Me_3SiCl	SEM	265, 266
$BiCl_3$ + Na_3P	BiP	SEM, XPS, XRD, NMR	265
$Bi(NME_2)_3$ + $P(SiMe_3)_3$	BiP		all 265
MCl_3 + $P(SiMe_3)_3$ (M = Sb, As)	MP		
MCl + $As(SiMe_3)_3$ (M = Bi, Sb)	MAs		
$BiCl_3$ + $SbCl_3$ + $P(SiMe_3)_3$, 1:1:2	$BiSbP_2$		
InX_3 (X = Cl, Br, I) + $As(SiMe_3)_3$	InAs, 3Me_3SiX	XRD	267
InX_3 (X = Cl, Br) + $P(SiMe_3)_3$	InP, 3Me_3SiX	XRD	267
InI_3 + $P(SiMe_3)_3$	$I_3In{\cdot}P(SiMe_3)_3$	X-ray, NMR, TGA	267
$InCl_3$ + $P(SiMe_3)_3$, 2:1	$[Cl_2In_3P_3(SiMe_3)_2]_n$, $InCl_3{\cdot}2THF$	X-ray	268
$InCl_3$ + $tBu_2P(SiMe_3)$	$[\{(tBu_2P)_2InCl\}_2]$	X-ray	269
$RInCl_2$ + $tBu_2P(SiMe_3)$ (R = iPr, Me_3SiCH_2)	$[\{RIn(\mu\text{-}tBu_2P)Cl\}_2]$		270
$(Me_3SiCH_2)InCl_2$			
+ $P(SiMe_3)_3$	$[Cl(Me_3SiCH_2)InP(SiMe_3)_2]_2$	X-ray	271
+ $LiP(SiMe_3)_2$, 1:2	$[Me(Me_3SiCH_2)InP(SiMe_3)_2]_2$	X-ray	271
Ph_2InCl + $E(SiMe_3)_3$ (E = P, As)	$[Ph_2InE(SiMe_3)_2]_2$	X-ray	272
Bu_2InCl + $P(SiMe_3)_3$	$[Bu_2InP(SiMe_3)_2]_2 \rightarrow$ InP + In (400 °C)	XRD	258

Table 21. (continued)

	products	analysis	ref
$(Me_3SiCH_2)_2InCl$			
+ $P(SiMe_3)_3$, 1:1	$[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$	X-ray	273
+ $P(SiMe_3)_3$, 2:1	$(Me_3SiCH_2)_2InP(SiMe_3)_2In(CH_2SiMe_3)Cl$	X-ray	273
$(Me_3CCH_2)_2InCl + LiP(SiMe_3)_2$	$Me(Me_3CCH_2)_2In{\cdot}P(SiMe_3)_3$		274
$RR'InCl + P(SiMe_3)_3$ or $LiP(SiMe_3)_2$ R = Cp*, R′ = Cl R = Me_3SiCH_2, R′ = Cl R = R′ = Me_3SiCH_2 R = R′ = Me_3CCH_2	$[RR'InP(SiMe_3)_2]_2$		275
$(Me_3SiCH_2)_3In + P(SiMe_3)_3$	$(Me_3SiCH_2)_3In{\cdot}P(SiMe_3)_3$	X-ray, TGA-DTA	263
$(Me_3CCH_2)_3In + E(SiMe_3)_3$ (E = P, As)	$(Me_3CCH_2)_3In{\cdot}E(SiMe_3)_3$	X-ray	274
$Bu_3In + P(SiMe_3)_3$	$Bu_3In{\cdot}P(SiMe_3)_3$ (130 °C) → $[Bu_2InP(SiMe_3)_2]_2$		258
$Me_3In + HP(SiMe_3)_2$	$[Me_2InP(SiMe_3)_2]_2$	XRD, X-ray	249
$(R)_2InP(SiMe_3)_2In(R)Cl + LiAs(SiMe_3)$ (R = CH_2SiMe_3)	$(Me_3SiCH_2)_3In{\cdot}As(SiMe_3)_3$	X-ray	276
$Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl + LiP(SiMe_3)$	$Ph_3Ga{\cdot}As(SiMe_3)_3$	X-ray	276
$[\{Cp(CO)_3Mo\}InCl_2] + P(SiMe_3)_3$	$[\{Cp(CO)_3Mo\}_4In_4(PSiMe_3)_4]$, In_4P_4-heterocubane skeleton (P, In alternating)	X-ray	277
$i$$PrInJ_2 + Li_2P{-}SiPh_3$	$[iPrInP(SiPh_3)]_4$, In_4P_4-heterocubane skeleton (P, In alternating)	X-ray	278
$i$$Bu_2AlH$, $H_2P{-}SiPh_3$	$[iBuAlP(SiPh)_3)]_4$, Al_4P_4-heterocubane skeleton (P, Al alternating)	X-ray	279

Table 22. Products of the Reaction of Different Silylphosphanes with Sulfur

silylphosphane	products without solvent	products with solvent
Me_3SiPMe_2 (**45**)	$(Me_3SiS)P(S)Me_2$ (**577**)	$Me_3SiSPMe_2$ (**585**)
$MeP(SiMe_3)_2$ (**41**)	$(Me_3SiS)_2P(S)Me$ (**578**) with small parts of S_8: $(Me_3SiS)(Me_3Si)PMe$ (**579**) $(Me_3SiS)_2PMe$ (**580**)	$(Me_3SiS)(Me_3Si)PMe$ (**579**) $(Me_3SiS)_2PMe$ (**580**)
$P(SiMe_3)_3$ (**4**)	$(Me_3SiS)_3P(S)$ (**581**) with small parts of S_8: $(Me_3SiS)(Me_3Si)_2P$ (**582**) $(Me_3SiS)_2(Me_3Si)P$ (**583**) $(Me_3SiS)_3P$ (**584**)	$(Me_3SiS)(Me_3Si)_2P$ (**582**) $(Me_3SiS)_2(Me_3Si)P$ (**583**) $(Me_3SiS)_3P$ (**584**)
$P_2(SiMe_3)_4$ (**185**)		$(Me_3Si)_2PP(SSiMe_3)(SiMe_3)$ (**586**) $(Me_3Si)(Me_3SiS)PP(SSiMe_3)(SiMe_3)$ (**587**) (diastereomere 4:1) $(Me_3SiS)_2PP(SiMe_3)_2$ (**588**) $(Me_3SiS)_2PP(SSiMe_3)(SiMe_3)$ (**589**) $(Me_3SiS)_2PP(SSiMe_3)_2$ (**590**) $(Me_3SiS)_3P(S)$ (**581**) $(Me_3SiS)_3P$ (**584**)

1:1 are the diphosphane **586** with one P−S bond in addition to the diphosphanes **587** and **588** with two P−S bonds and **581** with a P═S double bond. In a molar ratio of 1:2, the compounds **587** in addition to **586**, **588**, and **589** as well as $(Me_3SiS)_2PSiMe_3$ (**583**), $(Me_3SiS)_3P$ (**584**), $(Me_3SiS)_3P(S)$ (**581**), and P_4S_{10} were formed. A sulfur insertion into all four P−Si bonds is successful in a ratio of 1:3, yielding $(Me_3SiS)_2P{-}P(SSiMe_3)_2$ (**590**) in addition to **588**. Compounds **590** and **581** are the main products of the reaction in the molar ratio of 1:4 in addition to **584**, **589**, and P_4S_{10}. Even higher amounts of sulfur favor the formation of **581**, **590**, $(Me_3Si)_2S$, P_4S_3, and P_4S_7, whereas **581** decomposes according to (176).

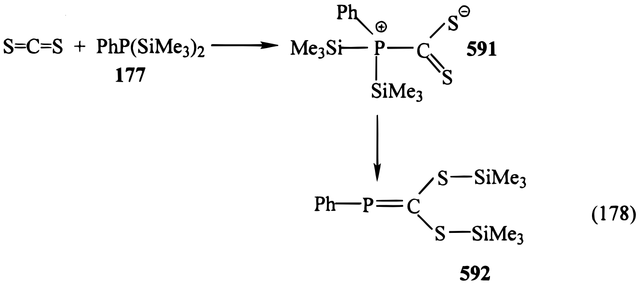
$$\underset{\textbf{581}}{4(Me_3SiS)_3P(S)} \rightarrow P_4S_{10} + 6(Me_3Si)_2S \qquad (176)$$

With HBr sulfur-containing silylphosphanes are destroyed at about −78 °C (177).[283]

$$\underset{\textbf{577}}{(Me_3SiS)P(S)} + HBr \rightarrow Me_2P(S)SH + Me_3SiBr$$

$$Me_2P(S)SH + HBr \rightarrow Me_2P(S)Br + H_2S \qquad (177)$$

CS_2 adds **177** under formation of the intermediate **591** and rearrangement of the Me_3Si groups, yielding the bis(trimethylsilylsulfano)methylidenephosphane (**592**) (178).[284]

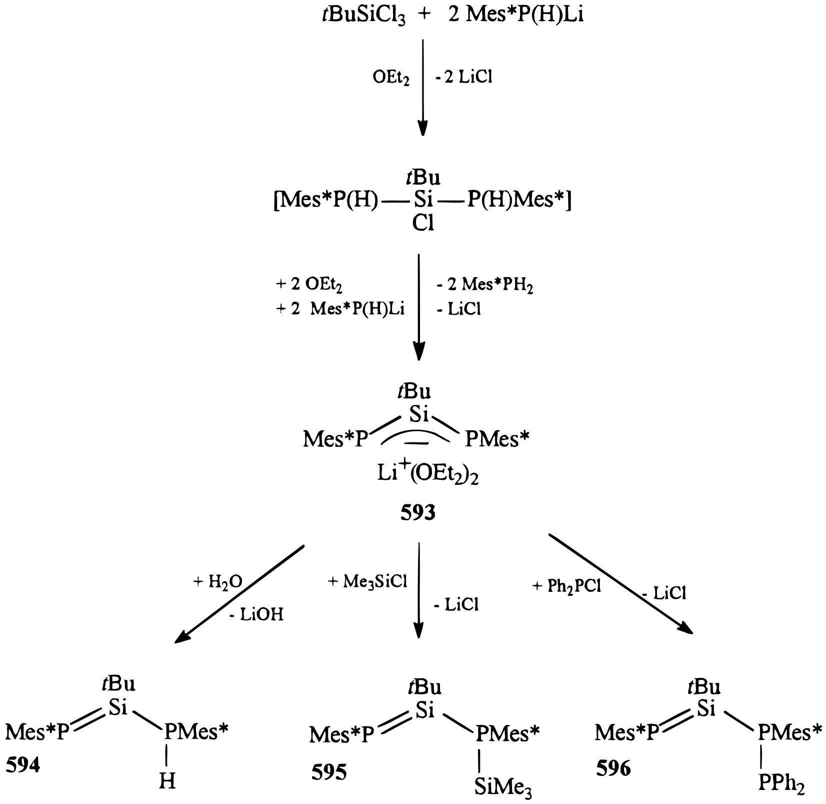


Further investigations in this field and reactions with phenylisothiocyanate are reported in a short overview about P−C−S multibond systems.[285]

XIV. Phosphasilenes and Phosphaalkenes

Compounds containing low-coordinated heavy main group elements are of current interest. Most of the

Scheme 40



efforts in this field were initiated and inspired by the developments in phosphorus and silicon chemistry. Syntheses of phosphaalkenes (P=C)[20] and phosphasilenes (P=Si) are closely linked with the development of silylphosphanes, and organosubstituted lithium phosphanides LiPR(SiR_3) turned out to be very useful reagents. An important aspect is the stabilization of the desired products by steric protection possible by means of sterically demanding organyl groups attached to silicon and phosphorus.

A. Phosphasilenes

1. Syntheses

Results from comprehensive investigations on preparation and reactivity of silenes (Si=C)[286] as well as silaimines (Si=N)[287] were essential for the development of the phosphasilene chemistry. The preparation of the first phosphasilenes $R'_2Si{=}PR$ (R = Mes, Es, Ph, Is, *t*Bu; R′ = Mes*, Is, Es, Mes, Phes) was achieved by HCl elimination from silylphosphanes $R'_2(Cl)SiP(H)R$, which are formed in the reaction of lithium phosphanides RP(H)Li with the corresponding dichlorosilanes R'_2SiCl_2. Several side reactions were encountered, for this reason, and because of the low stability of the phosphasilenes, their isolation in pure form was not achieved; nevertheless, they could be characterized by their ^{31}P NMR and ^{29}Si NMR data.[288,289]

An alternative route to phosphasilenes turned out to be the dilithiation of phospines RPH_2 with 2 equiv of *n*BuLi to $RPLi_2$ in the case of R = supermesityl (Mes* = 2,4,6-$tBu_3C_6H_2$) as the substituent on the P atom. Subsequent treatment with dichlorosilanes gave with lithium chloride the only and easily separable byproduct. This procedure is not applicable for primary phosphanes with a group smaller than Mes*.[289]

Thermal treatment of the lithium salt $tBu_2(F)Si{-}P[Li(THF)_3]tBu$ (**350**) (see (116)), the crystal structure of which has been determined by a X-ray-structure analysis,[290a] leads to the four-membered ring $[tBu_2Si{-}PtBu]_2$ (**325i**)[290b] via the phosphasilene $tBu_2Si{=}PtBu$. It could not be isolated, but was monitored by ^{31}P NMR data.[290a]

Treatment of $tBuSiCl_3$ with 4 equiv of Mes*PHLi in a one pot reaction yields the 1,3-diphospha-2-silaallyl anion, the lithium salt of which could be isolated as dieter adduct **593** in the form of deep red crystals (Scheme 40). In the presence of traces of moisture, **593** is immediately converted into the phosphino derivative **594**. Reactions of **593** with trimethylchlorosilane and diphenylchlorophosphine, respectively, afforded the thermally unstable P=Si−P−Si double bond system **595** and the yellow solid **596**, which was the first crystalline phosphasilene. The constitutions of **594**−**596** were determined by their NMR spectra, and of **596** additionally by a X-ray analysis.

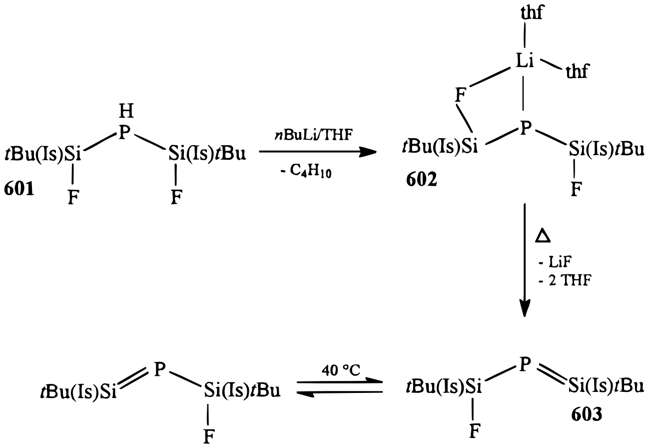
The X-ray structure analysis of **593** displays that in the solid state this compound is an η^2-lithio-1,3-diphospha-2-silaallyl system. The position of the lithium is in the P−Si−P plane and very short P−Si distances (211 pm; sum of the covalent radii for a single bond, 224 pm) have been determined.[291]

In the attempt to synthesize the P-silyl-substituted $tBu_2Si{=}P{-}SitBu_3$, the formation of $tBu_2Si(F){-}P(Li){-}$

Si*t*Bu$_3$ (**597**) was described as a preliminary stage. Compound **597** is formed by lithiation of *t*Bu$_2$Si(F)−P(H)−Si*t*Bu$_3$ (**598**), which is accessible by thermally induced elimination of LiF from *t*Bu$_2$SiF$_2$ and Li(H)P−Si*t*Bu$_3$ (**599**). Thermolysis of **597** leads in the presence of either Li(H)P−Si*t*Bu$_3$, isobutene, or butadiene, respectively, to products the formation of which can be understood as resulting from an addition of the reactants to the intermediately formed *t*Bu$_2$Si=P−Si*t*Bu$_3$.[292]

Whereas (*t*Bu)(Is)Si=PMes* (**600**)[289] is stable up to 60 °C, the thermal stability considerably increases in the phosphasilenes Is$_2$Si=PR (R = SiMe$_2$*t*Bu-Si(*i*Pr)$_3$, P*t*Bu$_2$; Is = 2,4,6-*i*Pr$_3$C$_6$H$_2$), which were accessible as pure orange oils (^{31}P NMR). Its formation proceeded analogously to that of *t*Bu$_2$Si=P*t*Bu[290] and *t*Bu$_2$Si=P−Si*t*Bu$_3$.[292,293] Starting from the bulkily substituted bis(fluorosilyl)phosphane (*t*Bu)(Is)FSi−P(H)−Si(F)(Is)(*t*Bu) (**601**), which was converted to the lithium phosphanide **602** by reaction with *n*BuLi, the phosphasilene **603** could be obtained by elimination of LiF (Scheme 41). The derivative **603** undergoes an 1,3-sigmatropic shift (fluctional behavior) of the fluorine atom above 40 °C.

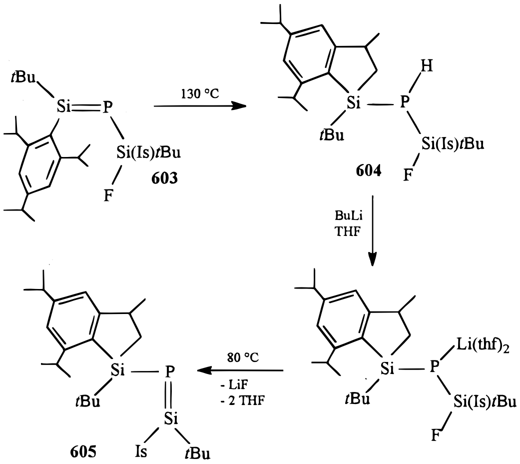
Scheme 41



Compound **603** crystallizes from hot toluene as pale yellow cubes. The crystal structure analysis resulted in P−Si distances of 205.3(2) and 220.7(2) pm, proving the presence of an isolated Si=P bond. This result is in agreement with ^{31}P NMR investigations as well as ab initio calculations on H$_2$Si=P−SiH$_2$F.[294]

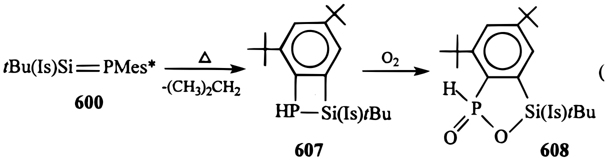
Compared to other phosphasilenes, compound **603** is thermally considerably more stable. Only at 130 °C will the procedure in Scheme 42 be initiated. The structures of the compounds **604** and **605** have been established spectroscopically as well as crystallographically.[295]

Scheme 42



2. Reactions

Already in the beginning of the chemistry of phosphasilenes, studies of their chemical behavior and reactivity were investigated. The reactivity pattern of **600** reflects the polarization as expected on the basis of electronegativities: phosphorus is the negative end of the Si=P dipole and adds electrophiles, whereas nucleophiles attack at silicon. In this way, **600** adds H$_2$O, D$_2$O, HCl at the double bond, leading for example to Mes*(H)P−Si(Cl)(*t*Bu)(Is) (**606**), which is cleaved to form Mes*PH$_2$ and (*t*Bu)(Is)SiCl$_2$ with an excess of hydrogen chloride. Also chalcogenes such as sulfur, selenium, and tellurium were added to form unstable three-membered ring compounds. Upon heating a solution of **600** in benzene or toluene to 60 °C, isobutene was eliminated with the formation of the phosphasiletene **607** (179). With elementary oxygen an insertion into the Si−P bond and a P-oxidation was observed, yielding the five-membered ring **608**.[289]



(179)

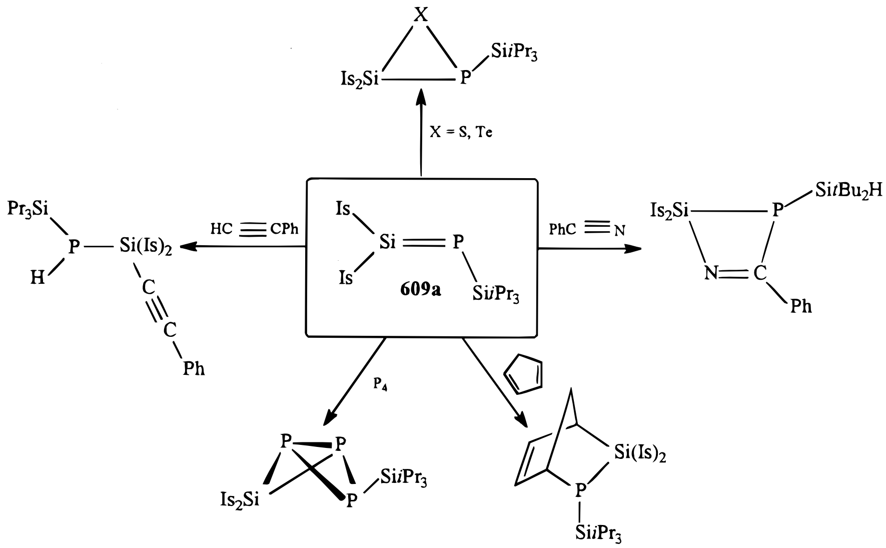
Starting from the monomeric lithium(fluorosilyl)phosphanides Is$_2$(F)Si−P[LiL$_n$]R (L = THF, n = 2, 3; R stands for eight different silyl groups), the corresponding phosphasilenes were synthesized and the reactivity of the representative derivative Is$_2$Si=P−Si*i*Pr$_3$ (**609a**) was studied. All reactions shown in Scheme 43 proceed by additions to the Si=P bond.

The reactions with the ketone O=CPh$_2$ and PhC(O)−C(O)Ph and with MesN$_3$ proceed in a widely analogoues way. The **609a** analogoues arsasilene Is$_2$Si=As−Si*i*Pr$_3$ show a corresponding behavior.[296,297]

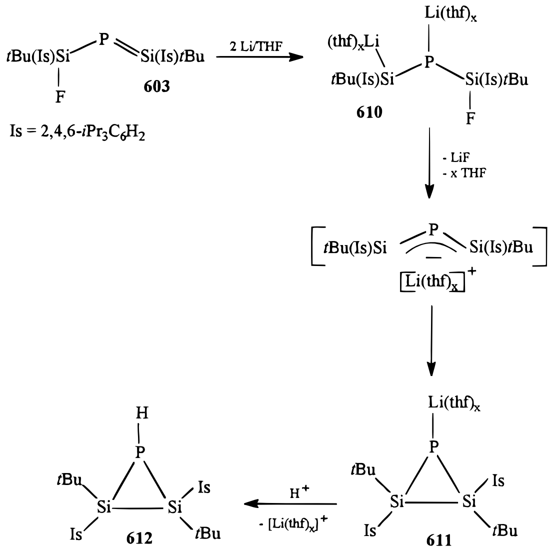
Addition of lithium to the Si=P bond takes place in the reaction with **603** at room temperature, yielding the extremely reactive intermediate **610**. Gentle warming of **610** to 40 °C initially leads by elimination of LiF to the three-membered ring compound **611**, the protonation of which yields the derivative **612**. The conversion of **610** to the ring compound **611** most likely occurs via the 1,3-disila-2-phosphaallyl anion (Scheme 44).[294]

In the analogous reduction of **609** (R$_3$ = *i*Pr$_3$ (**a**), Ph$_2$Me (**b**)) with 2 equiv of lithium metal (Scheme-

Scheme 43

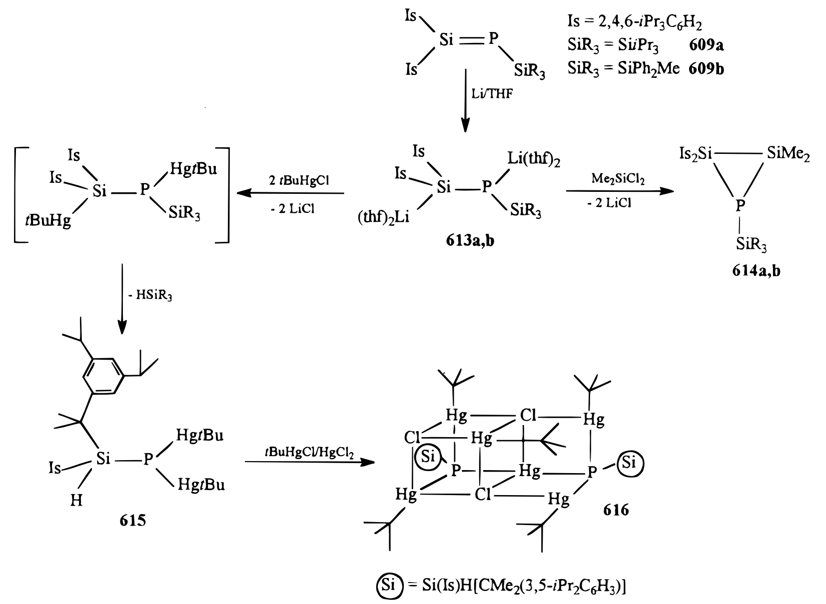


Scheme 44

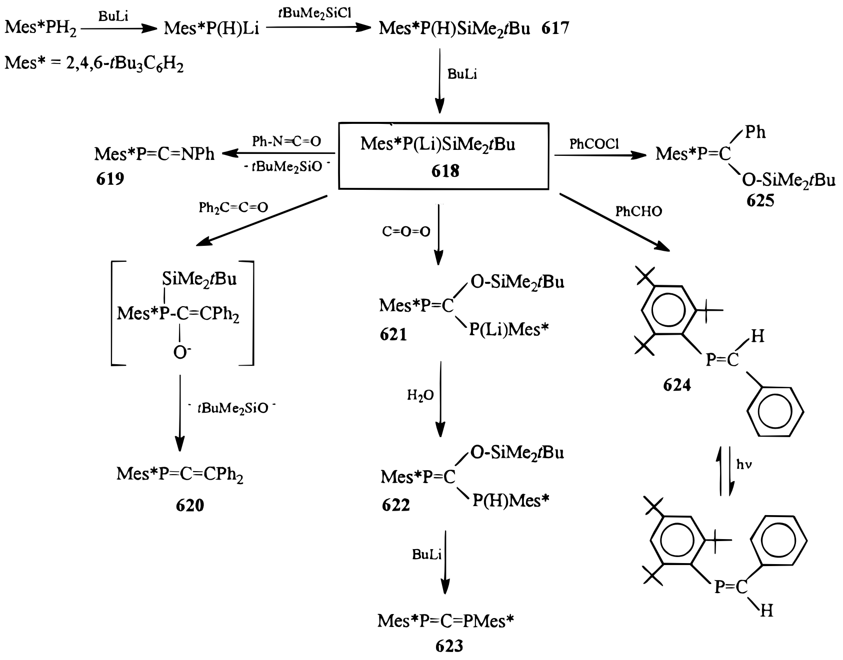


45), the corresponding lithiumsilaneidyl–lithiumsilylphosphanides **613a** and **613b** are formed, which have been isolates as yellow solids. Attempts to obtain crystals by complexation of the Li cations with 12-crown-4 or cryptand were not successful, but the constitution of these compounds is established by extensive NMR spectroscopy (^1H, ^{31}P, ^7Li, ^{29}Si) and derivatization with e.g. H_2O and LiOD, respectively. The reactivity of the phosphanides **613a**,**b** opens a new synthetical route to silaphospha-heterocycles. The cyclocondensation reaction with Me_2SiCl_2 yields the disilaphosphacyclopropane derivatives **614a**,**b**, respectively. The transmetalation product **615** (colorless crystals, sensitive toward light and moisture), furnished in the reaction of **613a**,**b** with *t*BuHgCl via rearrangement processes, reacts with *t*BuHgCl/$HgCl_2$ to a molecular aggregate **616** containing a $P_2Hg_6Cl_3$ framework, which can be regarded as a Lewis acid–base complex of a mercuriophosphane chelate ligand and $HgCl_2$. Each tetrahedral P atom is coordinated by a Si atom and three Hg atoms. Both compounds

Scheme 45



Scheme 46



615 and **616** have been characterized by extensive NMR analysis, **616** additionally by single crystal X-ray analysis, which doubtless demonstrates the topology of this molecule.[298]

B. Phosphaalkenes

1. Synthesis

Synthetical routes to compounds containing a P═C double bond are comprehensivly reviewed by Appel.[20] As mentioned, silylphosphanes have proved to be helpful building blocks in the preparation of such phosphorus compounds. In this chapter reactions of the basing metalated silylphosphane Mes*P(Li)SiMe$_2$*t*Bu (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) (**618**) with compounds including a C═O bond as ketones, aldehydes, and isocyanates following the principle of the Peterson reaction will be reported.[299] As demonstrated in Scheme 46, **618** could be prepared by lithiation of the bulkily substituted phenylphosphane Mes*PH$_2$ with BuLi, followed by silylation with *tert*-butyldimethylchlorosilane and repeated lithiation with butyllithium. If **618** was allowed to react with phenylisocyanate, diphenylketene,[300] benzaldehyde,[301] carbon dioxide,[302] and benzoyl chloride,[303] respectively, the phosphaalkenes in Scheme 46 were formed. All thus derivatives could be purified by means of column chromatography. The heterocumulene **619** is thermally very stable and monomeric even at room temperature. The colorless crystals of phosphaallene **620** are extraordinarily stable toward heat, light, atmospheric moisture, or oxygen.[300] When the E isomer **624** was irradiated with a mercury lamp for several hours, the isomerization reaction was observed to give an equilibrium mixture of E and Z isomers.[301] In the same procedure, **625** was isomerized to give the Z isomer. X-ray structure analyses of the phosphaalkene **620**,[304] of both isomers of **624**,[305] and of the Z isomer of **625**[304] were carried out.

XV. Abbreviations

Bu	butyl
Cy	cyclohexyl
DME	dimethoxyethane
Es	2,4,6-triethylphenyl
Et	ethyl
Is	2,4,6-triisopropylphenyl
Me	methyl
Mes	2,4,6-trimethylphenyl
Mes*	2,4,6-tri-*tert*-butylphenyl
OTf	trifluoromethylsulfonyl
Ph	phenyl
Phes	2,4,6-triphenylphenyl
Pr	propyl
THF	tetrahydrofuran
THP	tetrahydropyran
Xyl	2,6-dimethylphenyl

XVI. Acknowledgments

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