# Silylated Heptaphosphanes : Syntheses and Reactions

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Carried out under the supervision of Prof. Dr. Karl Hassler at the Institute of Inorganic Chemistry, TU Graz, from Februar 2007 to July 2010

“The Ultimate answer to Life, the Universe and Everything is...

(You're not going to like it...) Is...42

Which suggests that what you really need to know is 'What was the Question?”

(Douglas Adams, *The Hitchhiker's Guide to the Galaxy*)

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# 1 Introduction

The tricyclic cage of the heptaphosphanide anion $[P_7]^{3-}$ is a structural unit which is interesting and most important for solid state and molecular chemistry. A variety of substituents R such as $C_nH_m$ (Me, Et, Bu, i-Pr, benzyl), $SiMe_3$, $SiPh_3$ and $Si^tBu_3$, $SnPh_3$, $GePh_3$ or $PbPh_3$ (Ph = $C_6H_5$) as well as phosphino groups have been introduced into the $P_7$-system over the last thirty years.

There are numerous examples of relatively stable polyphosphorus anions that can be isolated, which contrasts with a relatively small number of isolable neutral hydrogen polyphosphanes which are inherently unstable. Further studies revealed that alkyl group transfer between anions allowed the preparation of partially alkylated species $[R_2P_7]^-$ and $[RP_7]^{2-}$, and that the reaction of $P_7(SiMe_3)_3$ with n-BuLi resulted in the formation of $[P_7(SiMe_3)_2]^-$. The first crystal structure of an alkylated anion $[R_2P_7]^-$ (R = benzyl) was reported not before 1998.

Two methods commonly are used for the preparation of these species. First, melts of the composition $K_3P_7$ can be used by fusing the elements at ~1000°C in sealed tubes, a procedure for which special equipment is needed. Moreover, it is extemely dangerous because polypnictides are known to spontaneously detonate even under anaerobic conditions, making this method not very attractive for preparative purposes. However, the use of the pure Zintl phases allowed the preparation and structural characterization not only of derivatives $P_7R_3$, but also of $[H_2P_7]^-$, $[HP_7]^{2-}$, $[(C_6H_5CH_2)_2P_7]^-$.

The second method starts from elemental phosphorus. In a solvent such as dimethoxyethane, red or white phosphorus reacts with sodium/potassium alloy forming a non-stoichiometric phosphide $Na_xP/K_xP$ which gives excellent yields of $R_3P_7$.

The first main objective of this thesis was to find reaction pathways leading to the synthesis of novel cages $P_7R_3$, $P_7R'R_2$ (R' unlike R), with R and R' oligosilyl groups or organo groups.

The second objective was the investigation of reactions which proceed by SiP bond cleavage under formation of $[P_7R_2]^-$ and $[P_7R]^{2-}$ anions, using $KO^tBu$ or $LiO^tBu$. Relative reaction rates depending on the size of the substituents were also investigated.

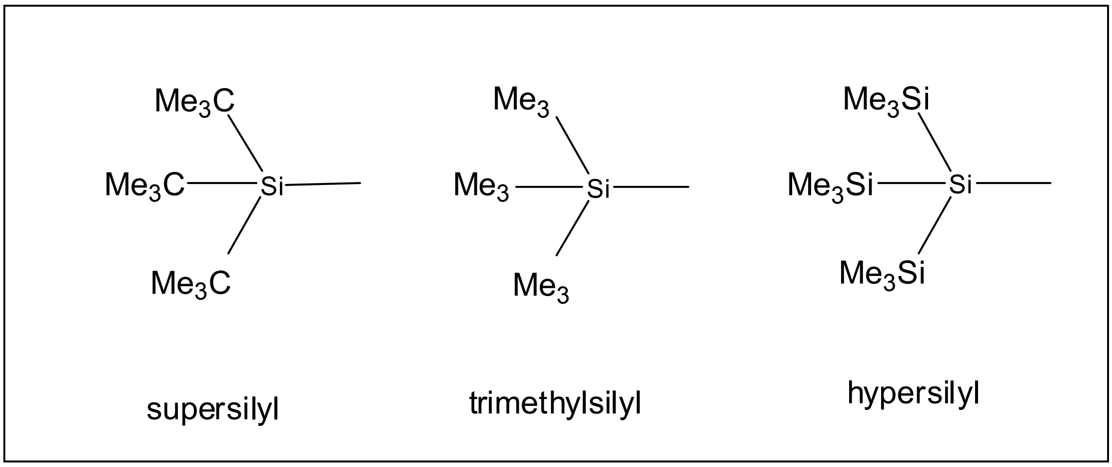
The last main objective was the exploration of reactions of the heptaphosphanides. Synthetic targets were cages bearing hydrogen atoms such as $HP_7R_2$, halogenated cages such as $BrP_7R_2$, and cages connected by a PP-bond or by a $(Si)_n$- and $(Sn)_n$-bridge.

# 2 Literature overview

## 2.1 Oligosilyl compounds of the elements N, P, As, Sb

### 2.1.1 Supersilyl compounds

Space demanding substituents play an important role in stabilizing elements in low oxidation states and give way to determine their frequently unusual molecular geometries.



Sterically overloaded supersilylated phosphanes and posphanide clusters were investigated by Nils Wiberg and co-workers. In addition to bis(supersilyl)tetraphosphane $({}^{t}\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_4$, tris(supersilyl)heptaphosphane $({}^{t}\mathrm{Bu}_3\mathrm{Si})_3\mathrm{P}_7$ [1,2] and tris(supersilyl)nonaphosphane $({}^{t}\mathrm{Bu}_3\mathrm{Si})_3\mathrm{P}_9$ [3] two unsaturated P=P containing

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[1] Wiberg, N.; Wörner, A.; Nöth, H.; Karaghiosoff, K.; Auner, N.; Weis, J. (Eds); *Organosilicon Chemistry* II, VCH, Weinheim, **1996**, S. 195.

[2] Kovács, I.; Baum, G.; Fritz, G.; Fenske, D.; Wiberg, N.; Schuster, H.; Karaghiosoff, K.; *Z. Anorg. Allg. Chem*. **1993**, 619, 453.

[3] Wiberg, N.; Woerner, A.; Lerner, H.-W.; Karaghiosoff, K.; Fenske, D.; *Eur. J. Inorg. Chem*. **1998**, 833.

phosphenides $[(Me_3C)_3Si]_2P_3Na$ [4] and $[(Me_3C)_3Si]_2P_4Na_2$ as well as polyphosphanides $[(Me_3C)_3Si]_4P_8Na_4$ and $[(Me_3C)_3Si]_3P_5Na_2$ [5] were prepared.

In those investigations, supersilyl groups were introduced by reactions of supersilyl radicals with white phosphorus, supersilyl anions with white phosphorus and with phosphorus trichloride, respectively.

Recently, another kind of tetraphosphanides $[(Me_3C)_3Si]_3P_4M_3$ (M = Li, Na) and $[(Me_3C)_2PhSi]_3P_4Na_3$ were synthesized by Lerner.[6]

### 2.1.2 Hypersilyl compounds

The tris(trimethylsilyl)silyl group, referred to as "hypersilyl" and abbreviated as "Hyp" (a term coined by Nils Wiberg to distinguish it from the tri(*tert*-butyl)silyl group which he named supersilyl) is one of the most frequently used bulky groups.

Lithium hypersilanide was first prepared in *situ* by Gilman and Smith in 1967 and later isolated and caracterized as solvates with tetrahydrofurane (THF), or 1,2-dimethoxyethane (DME). [7]

In 1998 Marschner developed a practical route to potassium hypersilanide by treatment of tetrakis(trimethylsilyl)silane with potassium *tert*-butanolate in THF.[8]

Due to its steric requirements,[9] interesting electronic properties,[10,11] and facile preparation, the hypersilyl group has been used for the synthesis of several novel classes of compounds such as silenes,[12] stannylenes, plumbylenes[13] and thus attracted much attention in the last decade. It was also used as substituent in

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[4] Wiberg, N.; Wörner, A.; Karaghiosoff, K.; Fenske, D.; *Chem. Ber*. Recueil, **1997**, 130, 125.

[5] Wiberg, N.; Wörner, A.; Lerner, H.-W.; Karaghiosoff, K. and Nöth, H.; *Z. Naturforschung*, **1998**, 53B, 1004.

[6] Lerner, H. –W.; Wagner, M.; Bolte, M.; *Chem. Commun*., **2003**, 990.

[7] Gilman, H.; Smith, C.; J. *Organomet. Chem.,* **1967**, 8(2), 245.

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[9] Frey, J.; Schottland, E.; Rappopot, Z.; Bravo-Zhivotovskii, D.; Nakash, M.; Botoshansky, M.; Kaftory, M.; Apeloig, Y.; *J. Chem. Soc. Perkin Trans.,* **1994**, 2555.

[10] Bock, H.; Meuret, J.; Ruppert, K.; *J. Organomet. Chem*., **1993**, 446, 113.

[11] Bock, H.; Meuret, J.; Ruppert, K. *Angew. Chem. Int. Ed. Engl*., **1993**, 32, 414.

[12] Apeloig, Y.; Korogodsky, G.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R.; *Eur. J. Inorg. Chem*. **2000**, 1091.

[13] Klinkhammer, K. W.; Schwarz, W.; *Angew. Chem*. **1995**, 107, 1448; *Angew. Chem. Int. Ed. Engl*. **1995**. 34. 1334.

transition metal element chemistry[14,15,16] and also in main group element chemistry.[17,18,19,20]

But despite the advantages the hypersilyl groups offers, only a small number of compounds with group V elements (N, P, As, Sb and Bi) are known.

The hypersilyl group, similar to the supersilyl group, should also stabilize polyphosphane or polyphosphanide clusters. The first hypersilyl-phosphorus-compound, HypP($^t$Bu)Cl was described by Cowley in 1982.[21] The compound is thermically stable up to 100°C due to the hypersilyl group.

Further well characterized hypersilyl stabilized phosphanes or phosphanides that have been reported to date are $(Me_3Si)_3SiPH_2$, $[(Me_3Si)_3Si]_2PH$, $[(Me_3Si)_3Si]_3P_7$,[22] Hyp$^t$BuPP$^t$BuHyp, HypPHK, $[HypPH]_2$, $[HypP(SiMe_3)]_2$ and $P_7Hyp_3$.[23, 24]

With nitrogen, $HypNH_2$, HypNHLi, $HypNH(SiMe_3)$ and $HypNLi(SiMe_3)$ have been described [25], and some derivatives such as tris(trimethylsilyl)silylamides of zinc [26], tin and mercury have also been reported.[27]

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[14] Arnold. J.; Tilley. T. D.; Rheingold. A. L.; Geib. S.; *Inorg. Chem.* **1987**, 26 (13), 2106.

[15] Piana. H.; Kirschgässner. U.; Schubert. U.; *Chem. Ber.* **1991**, 124 (4), 743.

[16] Meyer, J.; Willnecker, J.; Schubert, U.; *Chem. Ber.* **1989**, 122 (2), 223.

[17] Cowley, A. H.; Arif A. M.; Elkins, T. M.; *J. Organomet. Chem.* **1987**, 325 (1-2), C11.

[18] Cowley, A. H.; Arif A. M.; Elkins, T. M.; Jones, R. A.; *J. Chem. Soc. Chem. Commun.* **1986**, (24), 1776.

[19] Mallela, S. P.; Geanangel, R. A.; *Inorg. Chem.* **1991**, 30(7), 1480.

[20] Mallela, S. P.; Geanangel, R. A.; *Inorg. Chem.* **1990**, 29(18), 3525.

[21] Cowley, A.H.; Newman, T. H.; *Organometallics* **1982**, 1, 1412.

[22] Siegl H., Krumlacher W., Hassler K.; *Monatsh. Chem.* **1999**, 130, 139.

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[25] Westerhausen M., Schwarz W.; *Z. Anorg. Allg. Chem*. **1993**, 619, 1053.

[26] Westerhausen, M.; Wienecke, M.; Rademacher, B.; Schwarz, W.; *Chem. Ber./ Recueil* **1997**, 130, 1499.

[27] Westerhausen, M.; Greul, J.; Hausen, H. D.; Schwarz, W.; *Z. Anorg. Allg. Chem.* **1996**, 622, 1295.

### 2.1.3 Trimethylsilyl compounds

In the literature, many silylphosphanes (monophosphanes, cyclophosphanes, heptaphosphanes) carry the trimethylsilyl substituent for several reasons: the trimethylsilyl group is easily introduced in them, $SiMe_3Cl$ is cheap and $-SiMe_3$ is a good leaving group.

Nowadays, $LiP(SiMe_3)_2$ is the basic reagent for the formation of functional monophosphanes, diphosphanes, triphosphanes, and tetraphosphanes as well as of cyclic phosphanes with functional groups on selected P-atoms.[28, 29]

### 2.1.4 Other oligosilyl groups

A lot of other oligosilyl groups have been used in the past decades to synthesize silyl phosphorus compounds.

Examples include: $-SiMe_2Me_3$, $-SiMe(SiMe_3)_2$,[30] $SiPh(SiMe_3)_2$, $Si_6Me_{11}$, $SiPh_3$.[31]

Reactions of oligosilanes with phosphanides lead to cyclo- or polycyclophosphanes. The size and the bulkiness of the substituent on the silicium atom as well as the temperature play an important role in the formation of the rings. [30] Larger cycles are synthesized at higher temperature.[32]

The reactions of sodium/potassium phosphanide $Na_3P/K_3P$ with oligosilanes lead to polycyclic silylphosphanes with nortricyclene, bicycloheptane or bicyclooctane structure. Such system exist also with As, Sb and Bi.[33,34,35,36] Scheme 1 shows some examples of these reaction pathways.

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[28] Fritz, G.; Scheer, P.; *Chem. Rev.* **2000**, 100, 3341.

[29] Fritz, G.; *Adv. Inorg. Chem.* **1987**, 31, 171.

[30] Baudler, M.; Scholz, G.; *Angew. Chem*. **1989**, 101, 352.

[31] Mujica, C.; Weber, D.; v. Schnering, H. G.; *Z. Nafurforsch.* **1986**, 41b, 991.

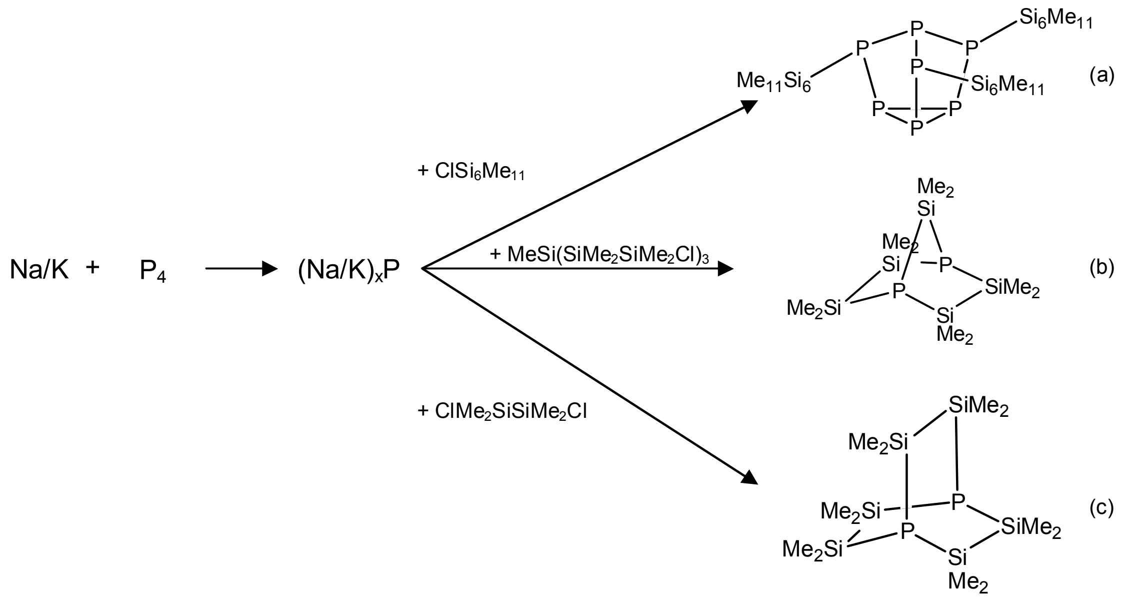
[32] Oakley, R. T.; Stanislawski, D. A.; West, R.; *J. Organomet. Chem.* **1978,** 157, 389.

[33] Hassler, K.; *Organosilicon Chemistry II; From Molecules to Materials,* (Eds. Auner, N.; Weis, J.), VCH, Weinheim, **1996,** 203.

[34] Hassler, K.; Seidl, S.; *J. Organomet. Chem.,* **1988,** 347, 27.

[35] Witt, J. D.; Thompson, J. W.; Durig, J. R.; *Inorg. Chem.* **1973,** 12, 811.

[36] Seidl, S.; *Diss.* TU Graz, **1987.**



**Scheme 1: P-Si bonding a[37] , b[38,39,40], c[41].**

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[37] Tekauz, G.; *Diss.* TU Graz, **2005.**

[38] Hassler, K.; *J. Organomet. Chem.* **1983,** 31, 246.

[39] Winkler, U.; Schieck, M.; Pritzkow, H.; Driess, M.; Hyla-Krispin, I.; Lange, H.; Gleiter, R.; *Chem. Eur. J.* **1997**, 3, 874.

[40] Kollegger, G. M.; Katzenbeisser, U.; Hassler, K.; Krüger, C.; Brauer, D.; Gielen, R.; *J. Organomet. Chem.* **1997,** 543(1-2), 103.

[41] Hassler, K.; Kollegger, G. M.; Siegl, H.; Klintschar, G.; *J. Organomet. Chem.* **1997,** 533, 51.

## 2.2 Synthetic methods leading to silicon-phosphorus compounds

The first silylphosphane $P(SiH_3)_3$ was obtained in 1953 by Aylett, Emeleus and Maddock [42] from the reaction of white phosphorus with iodosilane at 100°C. Later, Fritz synthesized the second representative of this class of substances $(SiH_3)PH_2$ which he prepared by thermal decomposition of $SiH_4$ in the presence of $PH_3$ in the gas phase at 450°C. [43]

The silylphosphanes can also be obtained by electric discharge in a gas mixture of silane and phosphane. For example, the compounds $SiH_3PH_2$[44], $(SiH_3)_2PH$[45], and $Si_2H_5PH_2$[46] were synthesized by this method.

Both methods require sophisticated equipment and are not well suited for preparative purposes.

Another method used for synthesizing this kind of compounds is the "salt elimination", where a metal phosphanide is added to a halogenated silane.

This technique was for the first time used by Kuchen and Buchwald in 1957 to synthesize trimethylsilyldiphenylphosphane by reaction of trimethylchlorosilane with sodium diphenylphosphanide (Scheme 2). [47]

$$Me_3SiCl + NaP(C_6H_5)_2 \longrightarrow Me_3SiP(C_6H_5)_2 + NaCl$$

**Scheme 2: Synthesis of trimethylsilyldiphenylphosphane.**

Diethyllithium phosphanide $LiPEt_2$ obtained as pure crystals by Issleib and Tzschach turned out to be a valuable base for the systematic synthesis of Si-functional silylphosphanes containing the $PEt_2$ group.

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[42] Aylett, B.J.; Emeleus, H.J.; Maddock, A.G.; *Research* **1953**, 6, 30 S.

[43] Fritz, G.; *Z. Naturforschung* **1953**, 8b, 776.

[44] Drake, J.E.; Jolly, W.L.; *Chem. and Ind.* **1962**, 1470.

[45] Gokhale, S.D.; Jolly, W.L.; *Inorg. Chem.* **1964**, 3, 1141.

[46] Gokhale, S.D.; Jolly, W.L.; *Inorg. Chem.* **1965**, 4, 596.

[47] Kuchen, W.; Buchenwald, H.; *Angew. Chem.* **1957**, 69, 307.

However, there is a second reaction path which is preferred if the silylphosphane contains more than one phosphanyl groups, which is a Li/H exchange (Scheme 3).

$$H_3SiPEt_2 + LiPEt_2 \longrightarrow H_2Si(PEt_2)_2 + LiH$$

$$HSi(PEt_2)_3 + LiPEt_2 \longrightarrow LiSi(PEt_2)_3 + HPEt_2$$

**Scheme 3: Typical synthesis of Si-functional silylphosphanes containing the $PEt_2$ group.**

Silylphosphanes can also be synthesized starting from elementary phosphorus. Basically the first step is the formation of sodium/potassium alloy to which elementary phosphorus is added to obtain a “Zintl” phase. A chlorosilane is then added to the mixture so that the desired product is formed.

The formation of tris(timethylsilyl)phosphane is a typical example for this pathway (Scheme 4).[48]

$$3\ Na/K + P_4 \longrightarrow (Na/K)_3P \longrightarrow P(SiMe_3)_3$$

**Scheme 4: Synthesis of tris(trimethylsilyl)phosphane starting from elementary phosphorus.**

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[48] Karsch, H.; Bienlein, F.; Rupprich, T.; Uhlig, F.; Herrmann, E.; Scheer, M.; *Synthetic Methods of Organometallic and Inorganic Chemistry*, (Ed. Karsch, H. H.), Thieme, Stuttgart, **1996**, 3, 58.

### 2.2.1 Forming P-P bonds

A number of reaction pathways are known in order to synthesize longer phosphorus chain compounds. Typical examples are shown in Scheme 5.

One possibility is the addition of a halogenophosphane to a phosphanide (Scheme 5, a).[49]

The coupling of two phosphanides using dibromoethane (Scheme 5, b) [50] or cleavage of the Si-P bond by $PR_2Cl$ leads to $P\text{-}PR_2$ (Scheme 5, c).

$(Me_3Si)_2PP(Me_3Si)_2$ can be synthesized directly from $Na_xP/K_xP$ and $Me_3SiCl$ (Scheme 5, d).

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$$R_2PX + R'_2PM \longrightarrow R_2P\text{-}PR'_2 + MX \qquad (a)$$

$$R'_2PM + BrCH_2CH_2Br \longrightarrow R'_2P\text{-}PR'_2 + MR \qquad (b)$$

$$R'_2PSiMe_3 + R_2PCl \longrightarrow R'_2P\text{-}PR'_2 + MR \qquad (c)$$

$$Na_XP/K_xP + Me_3SiCl \longrightarrow (Me_3Si)_2P\text{-}P(Me_3Si)_2 \qquad (d)$$

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**Scheme 5: Typical synthetic pathways leading to P-P bonds.**

### 2.2.2 Linking phosphorus atoms by a silyl or alkyl bridge

A very interesting reaction between $LiP(SiMe_3)_2$ and dimethyldichlorosilane is shown in Scheme 6. Dependent on the molar ratio, two different products were obtained, $(Me_3Si)_2PSiMe_2Cl$ (molar ratio 1:1) and $(Me_3Si)_2P\text{-}SiMe_2\text{-}P(SiMe_3)_2$ (molar ratio 2:1). The compound $(Me_3Si)_2PSiMe_2Cl$ containing one Cl atom can be purified by distillation without loss caused by Si-P cleavage. [51]

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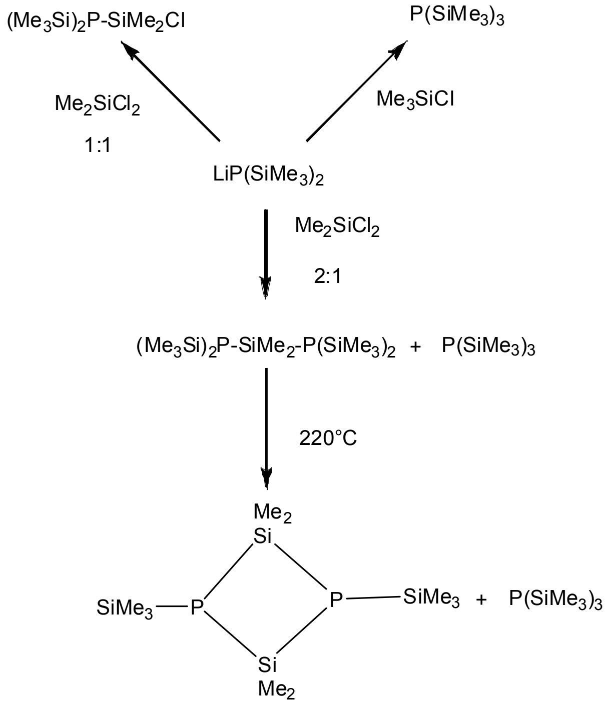
[49] Baudler, M.; Hallab, M.; Zarkadas, A.; Tolls, E.; *Chem. Ber*. **1973**, 106, 3962.

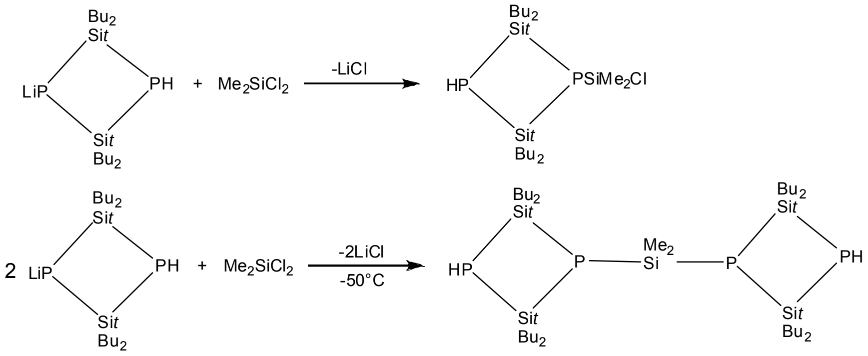
[50] Schumann, H; Roesch, L.; Schmidt-Fritsche, W.; *Chem. Ztg*. **1977**. 101(3), 156.

[51] Fritz, G.; Hölderich, W.; *Z. Anorg. Allg. Chem.* **1977**, 431, 76.



**Scheme 6: Reactions between $LiP(SiMe_3)_2$ and dimethyldichlorosilane.**

The reaction of $LiP(Si^tBu_2)_2PH$ with an excess of $Me_2SiCl_2$ led to $HP(Si^tBu_2)_2PSiMe_2Cl$.[52] The same reaction in a molar ratio 2:1 gave $HP(Si^tBu_2)_2PSiMe_2P(Si^tBu_2)_2PH$ (Scheme 7).[53]



**Scheme 7: Reaction of $LiP(Si^tBu_2)_2PH$ with an excess of $Me_2SiCl_2$.**

Another interesting result important for this work is the formation of tetrakis(trimethylsilyl)diphosphane from $LiP(SiMe_3)_2$ and $HgCl_2$ (Scheme 8).[54]

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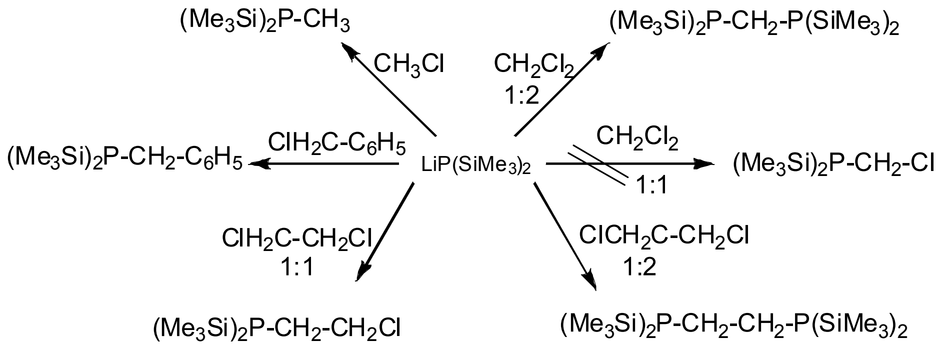
[52] Baudler, M.; Faber, W.; *Chem. Ber.* **1980**, 113, 3394.

[53] Parshall, G. W.; Lindsey, R. V.; *J. Am. Chem. Soc.* **1959**, 81, 6273.

$$LiP(SiMe_3)_2 + HgCl_2 \longrightarrow (Me_3Si)_2P\text{-}P(SiMe_3)_2 + P(SiMe_3)_3 + LiCl + Hg$$

**Scheme 8: Formation of tetrakis(trimethylsilyl)diphosphane.**

The use of various chlorinated hydrocarbons as shown below is also a good method to bridge two P-atoms (Scheme 9). [55, 51]



**Scheme 9: Synthetic pathways to bridge two P-atoms.**

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[54] Baudler, M.; Hofmann, G.; Hallab, M.; *Z. Anorg. Allg. Chem.* **1980**, 466, 71.

[55] Becker, G.; Mundt, O.; Rössler, M.; Schneider, E.; *Z. Anorg. Allg.Chem.* **1978**, 443, 42.

[51] Fritz, G.; Hölderich, W.; *Z. Anorg. Allg. Chem.* **1977**, 431, 76.

## 2.3 Cyclophosphanes

### 2.3.1 Monocyclic phosphanes

Cyclophosphanes are accessible from linear silylphosphanes which contain both Cl and $SiMe_3$ substituents by means of $Me_3SiCl$ elimination. 1,2-disubstituted or 1,4-disubstituted silylphosphanes yield cyclotetraphosphanes, whereas cyclotriphosphanes result from 1,3-disubstituted precursors.

### 2.3.2 Polycyclic phosphanes

The first polycyclic phosphane, $P_4H_2$ was reported in 1965 as one of the disproportionation products of diphosphane. [56] Then numerous binary phosphorus/hydrogen compounds of the general composition $P_nH_m$ ($m<n$) have been discovered, [57, 58, 59, 60, 61] together with the open-chain phosphanes $P_nH_{n+2}$. They were found in the distillation residues from the preparation of diphosphane, and the more phosphorus rich examples were found in the thermolysates of diphosphane .

Baudler and al. described many preparative routes to organopolycyclophosphanes. The synthetic pathways summarized below provide general accesses to polycyclic organophosphanes and have thus allowed major contributions to the development of this field to be made about 30 year s ago.

Compounds with the general composition $P_{x+y}R_z$ (x,y = number of organo-substituted and number of solely P-substituted phosphorus atoms, respectively) can be prepared by the routes shown in equations 1-4 (Scheme 10). [53, 62, 63, 64]

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[56] Baudler, M.; Stiindeke, H.; Borgardt, M.; Strabel, H.; *Naturwissenschaften* **1966**, 52, 345.

[57] Baudler, M.; *Pure Appl. Chem*. **1980**, 52,755.

[58] Bauler, M.; *Angew. Chem*. **1982**, 94, 520.

[59] Baudler, M.; *Angew. Chem.* **1987**, 99, 429; *Angew. Chem*., Int. Ed.Engl. **1987**, 26, 419.

[60] Baudler, M.; *ACS Symp. Ser.* **1981**, 171, 261.

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[62] Baudler, M.; Aktalay, Y.; Hahn, J.; Diur, E.; *Z. Anorg. Allg. Chem*. **1981**, 473, 20.

[63] Baudler, M.; Aktalay, Y.; Kazmierczak, K. ; Hahn, J.; *Z.Naturforsch*. **1983**, 38b, 428.

[64] Baudler, M.; Amdt, V.; *Z. Naturforsch.* **1984**, 396, 275.

$$(1)\quad xRPCl_2 + yPCl_3 + [(2x + 3y)/2]Mg \longrightarrow P_{x+y}R_x + [2x + 3y)/2]MgCl_2$$

$$(2)\quad (x/n)(PR)_n + yPCl_3 + (3y/2)Mg \longrightarrow P_{x+y}R_x + (3y/2)MgCl_2$$

$$(3)\quad xRPCl_2 + (y/4)P_4 + xMg \longrightarrow P_{x+y}R_x + xMgCl_2$$

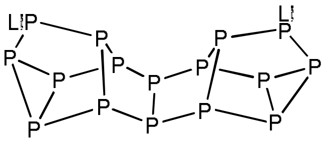
$$(4)\quad [(2x + 3y)/2n](PR)_n + yPCl_3 \longrightarrow P_{x+y}R_x + (3y/2)RPCl_2$$

**Scheme 10: Synthesis of polycyclic organophosphanes.**

Not only magnesium, but other dehalogenating agents such as alkali metals or lithium hydride may be used. In each case, the composition of the reaction product, that is the number of organosubstituted phosphorus atoms and the number of phosphorus atoms linked solely to other phosphorus atoms, can be predetermined by the molar ratio of the two phosphorus-containing starting materials. However a mixture of different compounds is always obtained which then must be separated.

A polyclyclic backbone very interesting for our work is $P_{16}R_2$. The structure of the phosphanide $P_{16}^{2-}$ is shown in Scheme 11.

Numerous non direct synthetic pathways are known giving hexadecaphosphanide as major final product.



**Scheme 11: Structure of the phosphanide $Li_2P_{16}$.**

The heptaphosphides $Li_2HP_7$ and $LiH_2P_7$ are not stable at room temperature and decompose in a complex disproportionation reaction to furnish, among others, dilithium hexadecaphosphanide. [52]

Dilithium hexadecaphosphanide $Li_2P_{16}$ can be obtained simply and in good yield by nucleophilic cleavage of white phosphorus with lithium dihydrogen phosphanide in a

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[52] Baudler, M.; Faber, W.; *Chem. Ber.* **1980**, 113, 3394.

molar ratio of 1.92:1 (Scheme 12).[65] The corresponding sodium salt can be obtained analogously using sodium in presence of 18-crown-6.[66]

$$23P_4 + 12LiPH_2 \longrightarrow 6Li_2P_{16} + 8PH_3$$

**Scheme 12: Synthesis of $Li_2P_{16}$ from white phosphorus.**

In 2006 Milyukov et al. used butyllithium for the metalation of $P_7H_3$. They found the formation of several polyphosphorus products including $Li_2P_{16}$.[67]

From sodium heptaphosphanide $Na_3P_7$ and $Ph_4P^+Cl^-$, $(Ph_4P)_2P_{16}$ was formed via disproportionation. The crystal structure of the salt was also reported.[68]

Formation of $Li_2P_{16}$ was also observed in the reaction of white phosphorus with $LiP(SiMe_3)_2$.[69, 70, 71]

A major problem associated with the synthesis of $[P_{16}]^{2-}$ is the lack of selectivity of the reaction. In 1996 Guérin and Richeson found a synthetic pathway using white phosphorus $P_4$ and K, treating the obtained mixture of polyphosphanides with ethanol.[72]

Interestingly, the reactions of tosylate ROTs with R = *cyclo*-$C_6H_{11}$ or *p*-$^tBuC_6H_4$ with $Na_3P_7$ didn't lead to the corresponding neutral heptaphosphanes but gave disodium hexadecaphosphanide $Na_2P_{16}$ as major product. The reaction of $Na_3P_7$ with one equivalent of an aryl tosylate with R = *o*-$MeC_6H_4$ and *p*-$MeC_6H_4$ also led to $Na_2P_{16}$.[73]

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[65] Fritz, G.; Hoppe, K. D.; Hönle, W.; Weber, D.; Mujica, C.; Manriquez, V.; v. Schnering, H. G.; *J. Organomet. Chem.* **1983**, 249, 63.

[66] Hönle, W.; v. Schnering, H. G.; *Z. Anorg. Allg. Chem*. **1978**, 440, 171.

[67] Milyukov, V. A.; Kataev, A. V.; Sinyashin, O. G.; Hey-Hawkins, E.; *Rus. Chem. B.* **2006**, 55(7), 1295.

[68] v. Schnering, H. G.; Hönle, W.; *Chem. Rev.* **1988**, 88, 243.

[69] Fritz, G.; Hirer, J.; Stoll, K.; Vaahs, T.; *Phosphorus Sulfur.* **1983**, 18, 65.

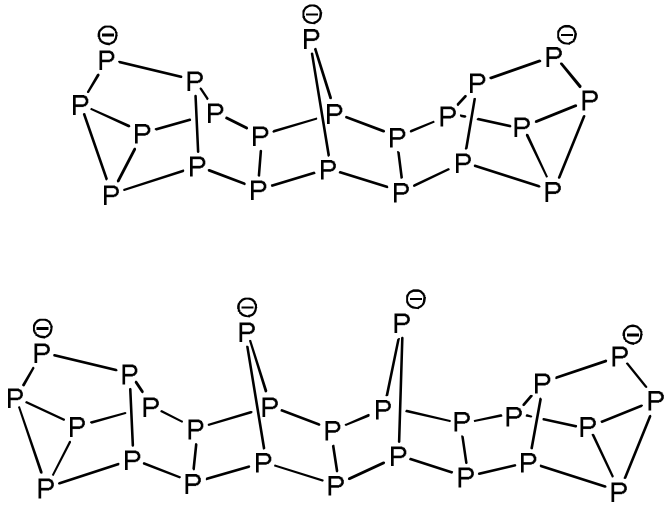
[70] v. Schnering, H. G. Angew. Chem. **1981**, 93, 44; *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 33.

[71] v. Schnering, H. G.; Manriquez, V.; Hönle, W.; *Angew. Chem.* **1981**, 93, 606; *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 594.

[72] Guérin, F.; Richeson, D.; *Inorg. Chem*. **1995**, 34, 2793.

[73] Milyukov, V. A.; Kataev, A. V.; Hey-Hawkins, E.; Sinyashin, O. G.; *Rus. Chem. B.* **2007**, 56(2), 298.

The cleavage of white phosphorus by lithium dihydrogen phosphanide or sodium under different stochiometric conditions also gave rise to the henicosaphosphanides $M_3P_{21}$ and to hexacosaphosphanide $M_4P_{26}$ with M=Li, Na, K. [74], [75] Structures of $M_3P_{21}$ and $M_4P_{26}$ are shown in Scheme 13.



**Scheme 13: Structure of $M_3P_{21}$ and $M_4P_{26}$.**

### 2.3.3 Adamantanes

One group of cyclophosphanes, the adamantanes can be obtained by reacting $Me_2SiCl_2$ with a mixture of the phosphanides $LiPH_2$, $Li_2PH$, and $Li_3P$ via several cyclic intermediates.

Also the thermal decomposition of linear and cyclic silylphosphanes yields stable products with an adamantane structure. With sterically very demanding groups P-P and Si-P rings of small size are formed preferably. [29]

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[74] Baudler, M.; Duster, D.; Langerbeins, K.; Germeshausen, J.; *Angew. Chem.* **1984**, 96, 309; *Angew. Chem., Int. Ed. Engl*. **1984**, 23, 317.

[75] Baudler, M.; Heumuller, R.; Duster, D.; Germeshausen, J.; Hahn, J.; *Z. Anorg. Allg. Chem*. **1984**, 518, 7.

[29] Fritz, G.; *Adv. Inorg. Chem.* **1987**, 31, 171.

## 2.4 Heptaphosphanes

### 2.4.1 Anionic compounds

One goal of this thesis is the synthesis of new stable heptaphosphanides and heptaphosphanes.

Among these, the tricyclic cage of the heptaphosphanide anion $[P_7]^{3-}$ is a structural unit which is interesting and most important for solid state and molecular chemistry. There are numerous examples of relatively stable polyphosphorus anions that can be isolated.

#### 2.4.1.1 Synthesis of $M_3P_7$

Alkali metal salts of phosphorus-containing compounds continue to be of considerable interest because of their synthetic value as transfer reagents and the structural diversity of their solid-state structures. Among the variety of the alkali metal phosphanides, numerous binary metal polyphosphanides containing isolated Zintl anions of the general formula $M_4P_6$ [76, 77, 78] $M_3P_7$ and $M_3P_{11}$ [79] were established since the early seventies.

A variety of methods were used for the preparation of these homopolyatomic anions. The syntheses and structural elucidations of metal phosphanides and polyphosphanides have been reviewed comprehensively by von Schnering and Hönle. [80]

Baudler et al. investigated the formation of $Li_3P_7$ by lithiation of $P_2H_4$ with $^nBuLi$ or $LiPH_2$ (Scheme 14). [81]

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[76] Abicht, H.-P.; Hönle, W.; v. Schnering, H. G.; *Z. Anorg. Allg. Chem*. **1984**, 519,7.

[77] Schmettow, W.; Lipka, A.; v. Schnering, H. G.; *Angew. Chem. Int. Ed. Engl*. **1974**, 13, 345.

[78] v. Schnering, H. G.; Meyer, T.; Hönle, W.; Schmettow, W.; Hinze, U.; *Z. Anorg. Allg. Chem*. **1987**, 553, 261.

[79] Meyer, T.; Hönle, W.; v. Schnering, H.G.; Z. Anorg. Allg. Chem. **1987**, 552, 69.

[80] v. Schnering, H. G.; Hönle, W.; *Chem. Rev*.; **1988**, 88, 243.

[81] Baudler, M.; Ternberger, H.; Faber, W.; Hahn, J.; *Z. Naturforsch.* **1979**, 34b, 1690.

$$P_2H_4 + 3\ {}^{n}BuLi \xrightarrow[-20^{\circ}C]{THF} Li_3P_7 + 11\ PH_3 + 3\ {}^{n}BuH$$

$$9\ P_2H_4 + 3\ LiPH_2 \xrightarrow[-20^{\circ}C]{DME} Li_3P_7 + 14\ PH_3$$

**Scheme 14: Formation of $Li_3P_7$ by lithiation of $P_2H_4$.**

Trilithium heptaphosphanide is most conveniently synthesized by nucleophilic cleavage of white phosphorus with an excess of lithium dihydrogen phosphanide in boiling DME. [52] This reaction gives $Li_3P_7$ in 95% yield (Scheme 15).

$$3\ P_4 + 6\ LiPH_2 \xrightarrow[boiling]{DME} 2\ Li_3P_7 + 4\ PH_3$$

**Scheme 15: Synthesis of $Li_3P_7$ by nucleophilic cleavage of white phosphorus.**

It is formed in the reaction of organolithium derivatives with white phosphorus also. [52] With higher amount of ${}^{t}BuLi$, the cycles $LiP_4{}^{t}Bu_3$ and $LiP_3{}^{t}Bu_2$ are formed, which can be silylated to give $P_4(SiMe_3){}^{t}Bu_3$ and $P_3(SiMe_3){}^{t}Bu_2$ by $Me_3SiCl$. [82]

In 1982 G. Fritz was the first who reported on the derivatization of $P_7(SiMe_3)_3$. The reaction of $P_7(SiMe_3)_3$ with BuLi, MeLi, ${}^{t}BuLi$ or $LiP(SiMe_3)_2$ yielded $Li_3P_7$, but the reactions were not fully understood. A mixture of degradation products including $P(SiMe_3)_3$, $LiP(SiMe_3)_2$ and $Li_3P_7$ was obtained.[83]

Trisodium heptaphosphanide $Na_3P_7$ was prepared in a good yield, with smaller amounts of higher polyphosphanides as by-products, by reaction of white phosphorus with sodium in diglyme in presence of a phase transfer catalyst (dibenzo-18-crown-6).[67]

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[52] Baudler, M.; Faber, W.; *Chem. Ber.* **1980**,113, 3394.

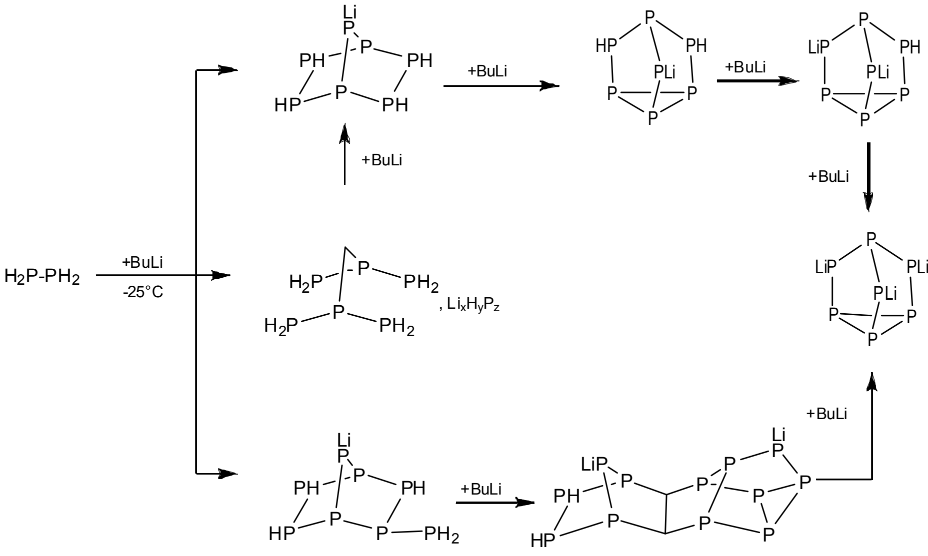
[82] Fritz, G.; Härer, J.; *Z. Anorg. Allg. Chem.* **1983**, 504, 23.

[83] Fritz, G.; Härer, J.; Scheider, K. H.; *Z. Anorg. Allg. Chem.* **1982**, 487, 44.

[67] Milyukov, V. A.; Kataev, A. V.; Sinyashin, O. G.; Hey-Hawkins, E.; *Rus. Chem. B.,* **2006**, 55(7), 1297.

### 2.4.1.2 Synthesis of $M_nP_7R_{m-n}$

Hydrogen polyphosphanides are intermediates between polyphosphanes and polyphosphanides. In contrast to the moderately stable, fully protonated polyphosphanes or the equally stable, fully deprotonated polyphosphanides, hydrogen polyphosphanides tend to form unstable solutions, forming dihydrogen monophosphanide and insoluble higher polyphosphanes via quick disproportionation. By deprotonation of diphosphane $H_2P\text{-}PH_2$ with *n*-butyllithium, hydrogen polyphosphanides may be prepared (Scheme 16). According to $^{31}$P-NMR data, this synthetic pathway yields a number of different anionic species after complicated rearrangement reactions. [84,85,86]



**Scheme 16: Synthesis of hydrogen polyphosphanides starting from $P_2H_4$.**

Several of these hydrogen polyphosphanides have been isolated in the pure state at low temperature.

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[84] Baudler M.; Heumüller, R.; Langerbeins, K.; *Z. Anorg. Allg. Chem*. **1984,** 514, 7.

[85] Baudler M.; Heumüller, R.; Düster, D.; *Z. Anorg. Allg. Chem.* **1993**, 619, 1007.

[86] Baudler M.; Heumüller, R.; *Z. Anorg. Allg. Chem.* **1988,** 559, 49.

The reductive cleavage of white phosphorus $P_4$ with an excess of alkali metals in liquid ammonia is also a method leading to hydrogen polyphosphanides. [87]

Korber and al. discovered the first stable hydrogen polyphosphanides $PPh_4H_2P_7$ in 1995. [88] In 2003 they reported on the crystal structure and a new pathway using an ion exchange resin loaded with protons leading to $PPh_4^+H_2P_7^-$. [89]

The compound $LiP_7(SiMe_3)_2$ resulted from the lithiation of the heptaphosphane $P_7(SiMe_3)_3$ with $Li_3P_7$ in a molar ratio 2:1. When a molar ratio 1:2 was used, a mixture of $LiP_7(SiMe_3)_2$ and $Li_3P_7$ could be isolated (Scheme 17). $Li_2P_7SiMe_3$ was not available [90]

$$2\,(SiMe_3)_3P_7 \; + \; Li_3P_7 \longrightarrow 3\,(SiMe_3)_2P_7Li$$

$$(SiMe_3)_3P_7 \; + \; 2\,Li_3P_7 \longrightarrow Li_3P_7 \; + \; (SiMe_3)_2P_7Li$$

**Scheme 17: Lithiation of $P_7(SiMe_3)_3$.**

Studies showed that alkyl group transfers between anions were facile and partially alkylated compounds $R_2P_7^-$, $RP_7^{2-}$ could be prepared by alkyl exchange reaction (Scheme 18).

$$2R_3P_7 \; + \; P_7^{3-} \longrightarrow 3R_2P_7^-$$

**Scheme 18: Alkyl exchange reaction.**

Although this method clearly gave the desired products, the reactions were hampered by redistributions of compounds. Pure partially alkylated polyphosphanides have not been isolated by this method.

In 1998, Mattamana discovered that trialkylammonium salts may serve as alkylating agents in reactions with $P_7^{3-}$ giving only the $R_2P_7^-$ dialkylated products.

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[87] Korber, N.; Aschenbrenner, J. C.; *J. Chem. Soc., Dalton Trans.* **2001**, 1165.

[88] Korber, N.; v. Schnering, H. G.; *J. Chem. Soc. Chem. Commun.* **1995**, 1713.

[89] Korber, N.; Aschenbrenner, J. C.; *Z. Anorg. Allg. Chem*. **2003**, 31.

[90] Fritz, G.; Härer, J.; Matern, E.; *Z. Anorg. Allg. Chem.* **1983**, 504, 38.

In this work they also reported on the first crystal structure of an alkylated anion $[R_2P_7]^-$ (R = benzyl).[91]

The reaction of $P_7^{3-}$ with alkylammonuim salts didn't give $P_7R_3$. These can be obtained using alkylhalides as described by Baudler and Fritz.[65] Even reactions of $P_7^{3-}$ with an excess of $R_4N^+$ gave quantitatively $[R_2P_7]^-$ where R= Me, Et and $^n$Bu (Scheme 19).[92]

$$Li_3P_7 \quad + \quad \text{excess } R_4N^+ \longrightarrow [R_2P_7]^- \quad + \quad 2R_3N$$

**Scheme 19: Reaction of $P_7^{3-}$ with an excess of $R_4N^+$.**

Starting from trisodium heptaphosphide, Milyukov synthesized $[R_2P_7]^-$ with R= $^i$Pr, $^i$Bu by action of the corresponding alkyl tosylates (Scheme 20).[73, 93]

$$Na_3P_7 \quad + \quad 2\ \text{R-O-Ts} \longrightarrow [R_2P_7]^- \quad + \quad 2\ \text{NaO-Ts}$$

**Scheme 20: Synthesis of $[R_2P_7]^-$.**

### 2.4.2 Neutral compounds

The first polycyclic organophosphane to be reported was trimethylheptaphosphane, prepared from the heptaphosphanide $Li_3P_7$ and methyl bromide (Scheme 21). Other heptaphosphanes were obtained anagously.[52, 81]

$$Li_3P_7 \quad + \quad 3MeBr \longrightarrow Me_3P_7 \quad + \quad 3LiBr$$

**Scheme 21: Synthesis of $Me_3P_7$.**

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[91] Mattamana, S. P.; Promprai, K.; Fettinger, J. C.; Eichhorn, B. W.; *Inorg Chem.* **1998**, 37, 6222.

[65] Fritz, G.; Hoppe, K. D.; Hönle, W.; Weber, D.; Mujica, C.; Manriquez, V.; v. Schnering, H. G.; *J. Organomet. Chem.* **1983**, 249, 63.

[92] Scott, C.; Fettinger, J. C.; Eichhorn, B. W.; *J. Am. Chem. Soc.* **1995**, 117, 5303.

[73] Milyukov, V. A.; Kataev, A. V.; Hey-Hawkins, E.; Sinyashin, O. G.; *Rus. Chem. B.*, **2007**, 56(2), 304.

[93] Milyukov, V. A.; Kataev, A. V.; Hey-Hawkins, E.; Sinyashin, O. G; *Phosphorus, Sulfur.* **2008**,183, 513.

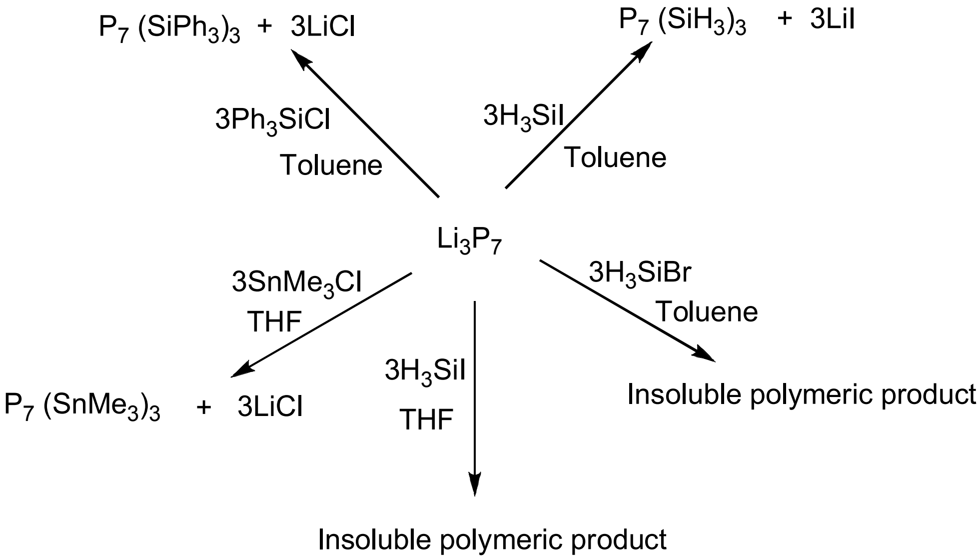
[52] Baudler, M.; Faber, W.; *Chem. Ber.* **1980**, 113, 3394.

[81] Baudler, M.; Ternberger, H.; Faber, W.; Hahn, J.; *Z. Naturforsch.* **1979**, 34b, 1690.

Whereas the synthetic methods described for the synthesis of cyclophosphanes provide general accesses to polycyclic organophosphanes, polycyclic silylphosphanes with a phosphorus skeleton usually result from the reactions of halosilanes with alkali metal phosphanides, for instance $M_3P_7$.[94,95]

Substituents such as $SiPh_3$ and $Si^tBu_3$, $Si_6Me_{11}$, $SnPh_3$, $GePh_3$ or $PbPh_3$ ($Ph=C_6H_5$) as well as phosphino groups have also been introduced into the $P_7$-system over the last twenty years.

In 1983 G. Fritz and von Schnering found synthetic pathways to $P_7(SiPh_3)_3$, $P_7(SiH_3)_3$ and $P_7(SnPh_3)_3$ starting from $Li_3P_7$ (Scheme 22).[65]



**Scheme 22: Synthetic pathways to $P_7(SiPh_3)_3$, $P_7(SiH_3)_3$ and $P_7(SnPh_3)_3$.**

Subsequent studies by Fritz and Schneider showed that several $R_3P_7$ species could be prepared by this method where R = $C_nH_{2n+1}$ (Me, Et, $^i$Pr), $SiMe_3$, $SnMe_3$, and $PbMe_3$.[89,96,97]

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[94] Baudler, M.; Faber, W.; Hahn J.; *Z. Anorg. Allg. Chem.* **1980**, 469, 15.

[95] Baudler, M.; Temberger, H.; Faber, W.; Hahn, J.; *Z. Naturforsch*. **1979**, 34b, 1690.

[65] Fritz, G.; Hoppe, K. D.; Hönle, W.; Weber, D.; Mujica, C.; Manriquez, V.; v. Schnering, H. G.; *J. Organomet. Chem.* **1983**, 249, 63.

[96] Fritz, G.; Schneider, H.-W.; *Z. Anorg. Allg. Chem.* **1990**, 584, 12.

[97] Kovacs, I.; Baum, G.; Fritz, G.; Fenske, D.; Wiberg, N.; Schuster, H.; Karaghiosoff, K.; *Z. Anorg. Allg. Chem.* **1993**, 619, 453.

Furthermore, the hexadecaphosphane $P_{16}R_2$ and the partially organo-substituted henicosaphosphane $P_{21}HMe_2$ were similarly accessible by direct alkylation of the corresponding polyphosphanides.

The $SiMe_3$-group is of prime importance. The derivative shows satisfactory stability, is easily purified, and is a valuable starting material for other $P_7$-based compounds due to the pronounced reactivity of the Si-P bonds.

In 1995 Schmidbaur and Bauer developed an efficient and less hazardous procedure to synthesize $P_7(SiMe_3)_3$ by using non inflammable red phosphorus, sodium and potassium alloy and $Me_3SiCl$, working in toluene instead of ether, glyme or tetrahydrofurane in the silylation step.[98]

$P_7H_3$ is formed by action of MeOH on $P_7(SiMe_3)_3$ (Scheme 23). [95]

$$(SiMe_3)_3P_7 \quad + \quad 3\ MeOH \quad \longrightarrow \quad H_3P_7 \quad + \quad 3\ MeOSiMe_3$$

**Scheme 23: Formation of $P_7H_3$ by action of MeOH on $P_7(SiMe_3)_3$.**

The readily accessible tris(trimethylsilyl)heptaphosphane $P_7(SiMe_3)_3$ [99] is in fact a suitable starting material for the synthesis of many hepaphosphanes. Its reaction with $R_3MCl$ (R= Me, Ph; M=Si, Ge, Sn, Pb) gave rise to heptaphosphanes of general formula $P_7(MR_3)_3$ (Scheme 24).

$$P_7\ (SiMe_3)_3 \quad + \quad 3\ R_3MCl \quad \rightleftharpoons \quad P_7\ (MR_3)_3 \quad + \quad 3\ Me_3SiCl$$

**Scheme 24: Synthesis of heptaphosphanes $P_7(MR_3)_3$.**

In 1986 von Schnering et al. synthesized $P_7(SiPh_3)_3$ by cleavage of the Si-P bond of $P_7(SiMe_3)_3$ by action of $ClSiPh_3$, $P_7(GePh_3)_3$ using $ClGePh_3$ and $P_7(SnPh_3)_3$ by action

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[98] Schmidbaur, H.; Bauer, A.; *Phosphorus, Sulfur.* **1995**, 102, 217.

[95] Baudler, M.; Ternberger, H.; Faber, W.; Hahn, J.; *Z. Naturforsch.* **1979**, 34b, 1690.

[99] Fritz, G.; Hölderich, W.; *Naturwiss.* **1975**, 573, 62.

of $ClSnPh_3$. [100] The reaction is influenced by the solubility of the products and educts. The driving force of the reaction is the lower solubility of the $P_7(MPh_3)_3$ compounds. Recently, V. A. Milyukov and Hey-Hawkins described a new way to $P_7R_3$ (with R an alkyl group) starting from $Na_3P_7$ using alkyl and aryl tosylates with R = Bu, $C_6H_{13}$, $^iBu$, $^iPr$, 3-$C_5H_{11}$ (Scheme 25). [73]

$$Na_3P_7 + 3\ R\text{-}O\text{-}Ts \longrightarrow P_7R_3 + 3\ NaO\text{-}Ts$$

**Scheme 25: Synthesis of $P_7R_3$ using alkyl and aryl tosylates.**

Silylated heptaphosphanes can also be synthesized directly from elementary phosphorus. For instance, tris(tri-tert-butylsilyl)heptaphosphane $P_7(^tBu_3Si)_3$ was formed in the reaction of $(^tBu)_3Si\text{-}Si(^tBu)_3$ with white phosphorus (Scheme 26).[101]

$$3(^tBu)_3Si\text{-}Si(^tBu)_3 + 3/2\ P_4 \longrightarrow 2P_7(^tBu_3Si)_3$$

**Scheme 26: Formation of $P_7(^tBu_3Si)_3$.**

Starting from $R_2P_7^-$ (R= Me, Et, $^nBu$) and by action of $ClCH_2Ph$, MeI, $^nBuBr$, Eichhorn and al. were able to prepare the heteroleptically substituted heptaphosphanes $(CH_2Ph)Me_2P_7$, $(CH_2Ph)Bu_2P_7$ and $MeBu_2P_7$. [91] No crystal structures were obtained.

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[100] Mujica, C.; Weber, D.; v. Schnering, H. G.; *Z. Naturforsch.* **1986**, 41B, 991.

[73] Milyukov, V. A.; Kataev, A. V.; Hey-Hawkins, E.; Sinyashin, O. G.; *Rus. Chem. B.* **2007**, 56(2), 304.

[101] Kovacs, I.; Baum, G.; Fritz, G.; Fenske, D.; Wiberg, N.; Schuster, H.; Karaghiosoff V. ; *Z. Anorg. Allg. Chem* **1993**, 619, 453.

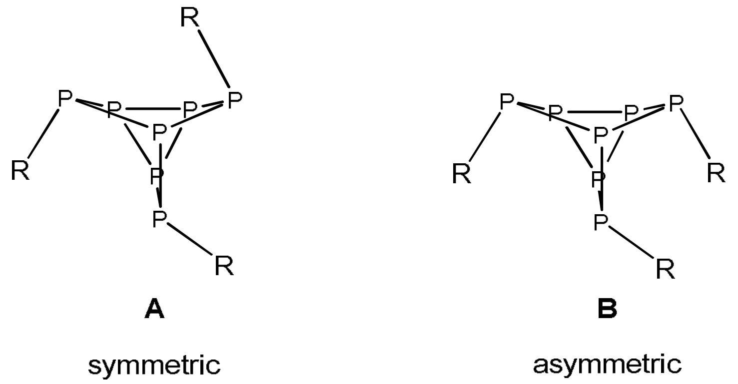
[91] Mattamana, S. P.; Promprai, K.; Fettinger, J. C.; Eichhorn, B. W.; *Inorg Chem.* **1998**, 37, 6222.

### 2.4.3 Halogenoheptaphosphanes

In 1994 Tattershall and Kendall reported on the reaction of $P_4$ with $Br_2$ or $I_2$. They could identify exo, exo-$P_4Cl_nBr_{2-n}$, exo, endo-$P_4Cl_nBr_{2-n}$, sym-$P_7X_3$ (X=Br, I) and $P_2X_nY_{4-n}$ (X and Y= Cl, Br, I) by NMR experiments, albeit in low concentation. They observed that in general the $P_7X_3$ structure was formed to a significant yield with iodine because the ligand is capable of supporting sufficient positive charge. [102]

### 2.4.4 Isomerism of heptaphosphanes and heptaphosphanides

The positions of the substituents R in $R_3P_7$-systems are important not only for their chemical properties and their reactivity, but also for the number of signals in the $^{31}$P-NMR spectrum. Two isomers, **A** and **B**, are possible, as shown in Scheme 27. Both isomers are chiral.



**Scheme 27: Structure of the two possible isomers of $R_3P_7$-systems.**

The organo-substituted heptaphosphanes $P_7R_3$ with small R always occur like the parent compound $P_7H_3$, as a mixture of the two configurational isomers **A** and **B** with the substituents in a symmetrical or asymmetrical orientation with regard to the $C_3$ axis of the nortricyclene skeleton. In the case of $P_7H_3$, the isomer ratio as determined by the signal intensities in the $^{31}$P-NMR spectrum more or less corresponds to the statistical value of **A/B** = 1:3 [103] whereas for $P_7Me_3$ it is clearly shifted in favor of the

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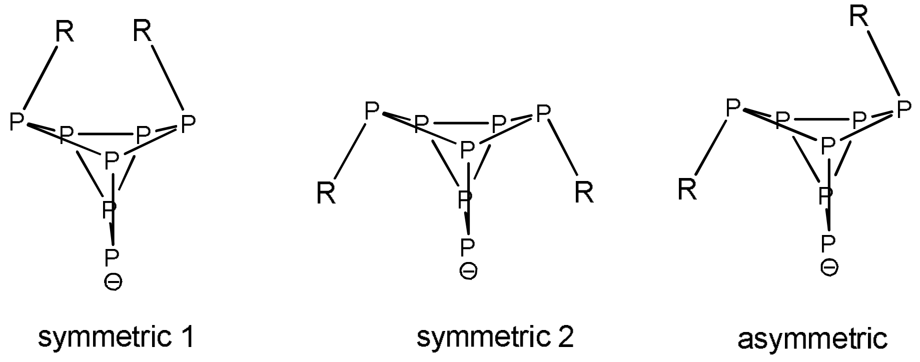
[102] Tattershall, B. W.; Kendall, N. L.; *Polyhedron* **1994** (13), 10, 1517.

[103] Baudler, M.; Riekehof-Böhmer, R.; *Z. Naturforsch.* **1985**, 40b, 1424.

symmetrical isomer, **A/B** = 1:1.8. [56, 104] This probably is due to steric interaction between the substituents which is larger if they are arranged asymmetrically to the $C_3$ axis in isomer **B.**

This tendency is more pronounced with larger alkyl groups (R = Et, $^i$Pr, $^n$Bu, $^i$Bu) [65] The symmetrical isomer **A** is formed exclusively in the cases of the sterically demanding substituents $R_3M$ (R = Me, Ph; M = Si, Ge, Sn, Pb) and $Fe(CO)_2Cp$. [67, 64, 30, 105]

Milyukov showed that the ratio of isomers of heptaphosphanides $R_2P_7^-$ substantially depends of the steric demands of the alkyl substituent ($^n$Bu, n-$C_6H_{13}$, $^i$Bu, $^i$Pr, $CHEt_2$, $Me_3Si$). The content of the symmetric isomer 2 is higher for the bulkier substituent. [73] The three isomers are schematized in Scheme 28



**Scheme 28: Structure of the three possible isomers of $MR_2P_7$-systems with M = K, Li.**

The lithium heptaphosphide $LiP_7(SiMe_3)_2$ can be extracted with toluene from the silylation reaction of $Li_3P_7$. Similarly, the isomers of $LiP_7R_2$ (R= Et, $^i$Pr, $^i$Bu) can be extracted from the mixture obtained by reaction of $Li_3P_7$ with alkylbromide. In solution at 20°C the symmetric isomers of $LiP_7R_2$ slowly form the asymmetric isomer, whereas the latter up to 70°C do not show any inversion. [73]

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[56] Baudler, M.; Stindeke, H.; Borgardt, M.; Strabel, H.; *Naturwissenschaften* **1966**, 52, 345.

[104] Baudler, M.; Pontzen, Th.; *Z. Naturforsch.* **1983**, 38b, 955.

[65] Fritz, G.; Hoppe, K. D.; Hönle, W.; Weber, D.; Mujica, C.; Manriquez, V.; v. Schnering, H. G.; *J. Organomet. Chem.* **1983**, 249, 63.

[67] Milyukov, V. A.; Kataev, A. V.; Sinyashin, O. G.; Hey-Hawkins, E.; *Rus. Chem. B.* **2006**, 55(7), 1295.

[64] Baudler, M.; Amdt, V.; *Z. Naturforsch.* **1984**, 396, 275.

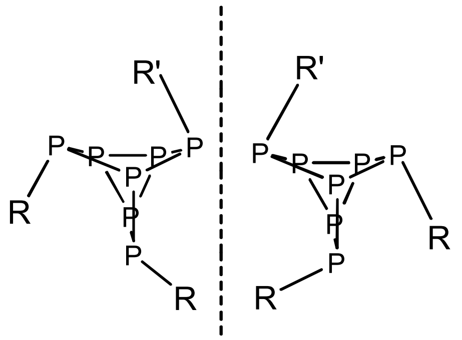
[30] Baudler, M.; Scholz, G.; *Angew. Chem.* **1989**, 101, 352.

[105] Weber, D.; Mujica, C.; v. Schnering, H. G.; *Angew. Chem.* **1982**, 94, 869.

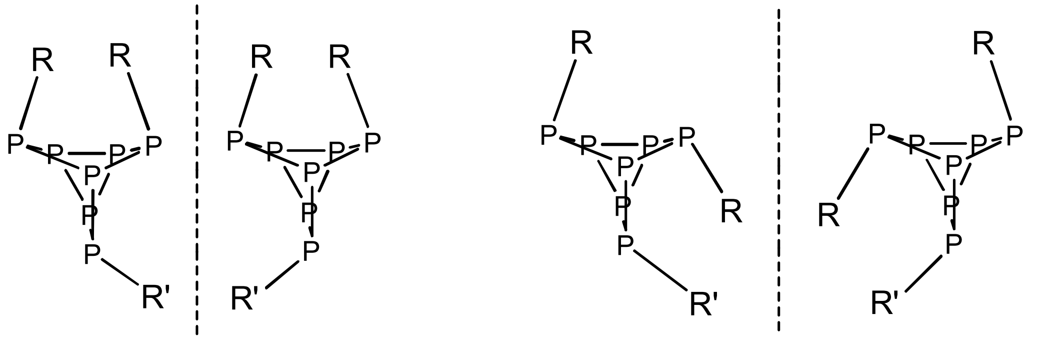
[73] Milyukov, V. A.; Kataev, A. V.; Hey-Hawkins, E.; Sinyashin, O. G.; *Rus. Chem. B.* **2007**, 56(2), 304;

Noteworthy $Li_2P_7R$ (R=$SiMe_3$ or aryl) is not available. [59]

For the heteroleptic heptaphosphanes $R'R_2P_7$ three enantiomeric pairs of symmetric and asymmetric isomers are potentially formed (Scheme 29). [118]



symmetric



asymmetric 1

asymmetric 2

**Scheme 29: Structure of the possible isomers of $R'R_2P_7$-systems.**

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[59] Baudler, M.; *Angew. Chem.* **1982**, 94, 520; *Angew. Chem., Int. Ed. Engl.* **1982**, 21, 492.

[73] Milyukov, V. A.; Kataev, A. V.; Hey-Hawkins, E.; Sinyashin, O. G.; *Rus. Chem. B.* **2007**, 56(2), 304.

# 3 Results and discussion

## 3.1 Synthesis of silylated heptaphosphanes

The stability of the heptaphosphanide $[P_7]^{3-}$ is well known and certainly reflects the tendency of phosphorus to accumulate negative charge. Consequently, derivatives such as $[RP_7]^{2-}$, $[R_2P_7]^-$ and $P_7R_3$ are expected to possess exceptional electronic stability for substituents R that are capable of supporting sufficient positive charge. A further kinetic stabilization of these species can be achieved if in addition R is a sterically demanding group. As both these properties can be found in oligosilyl groups, the aim of this work was to develop a method for the synthesis of oligosilylheptaphosphanes and to investigate their reactivities. The introduction of oligosilyl groups offers two further advantages which are not found in organoheptaphosphanes. First, SiP bonds can be cleaved at low temperatures with various reagents such as BuLi, $KO^tBu$ or $C_2Cl_6$ and second, SiSi bonds also can be cleaved at temperatures as low as -70°C, for instance with $KO^tBu$.

As explained in Section 2.1.3, the trimethylsilyl group $-SiMe_3$ is a very good leaving group. For this reason the heptaphosphane $P_7(SiMe_3)_3$ is a suitable starting material for the synthesis of heptaphosphanides as well as other silylated heptaphosphanes.

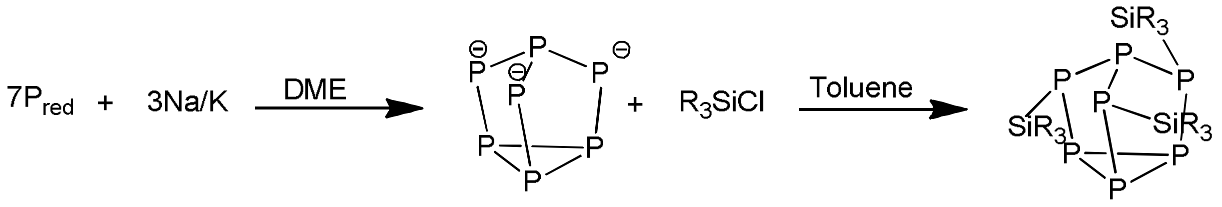
### 3.1.1 Synthesis of $P_7(SiMe_3)_3$

Polycyclic silylphosphanes with a pure $P_7$-skeleton result generally from the reactions of halosilanes with alkali metal phosphanides $M_3P_7$. Due to the utilisation of white phosphorus, these reactions are usually hazardous for the preparation of larger quantities. Schmidbaur and Bauer described a less hazardous and more efficient procedure starting from red phosphorus.[99] In this work, this procedure was followed for the synthesis of the different oligosilylheptaphosphanes $P_7(SiMe_3)_3$, $P_7[Si(SiMe_3)_3]_3$ and $P_7[SiMe(SiMe_3)_2]_3$.

---

[99] Schmidbaur, H.; Bauer, A.; *Phosphorus, Sulfur.* **1995**, 102, 217.

Heptaphosphanes were synthesised from $Na_xP/K_xP$ prepared from sodium/potassium alloy and red phosphorous in DME and in the last step by addition of a halogenated oligosilane. In this work the halogenated oligosilane always was a chlorosilane.



**Scheme 30: General pathway for the synthesis of silylheptaphosphanes $P_7(SiR_3)_3$.**

A typical $^{31}$P-NMR spectrum (Figure 1) of an oligosilylheptaphosphane shows three groups of signals with relative intensities 3:1:3. The signals of the three equatorial P-atoms bearing the $SiR_3$-groups give resonances around 0 ppm. The quartet from the apical P-atom appears at -100 ppm, and basal P-atoms around -150/-180 ppm.

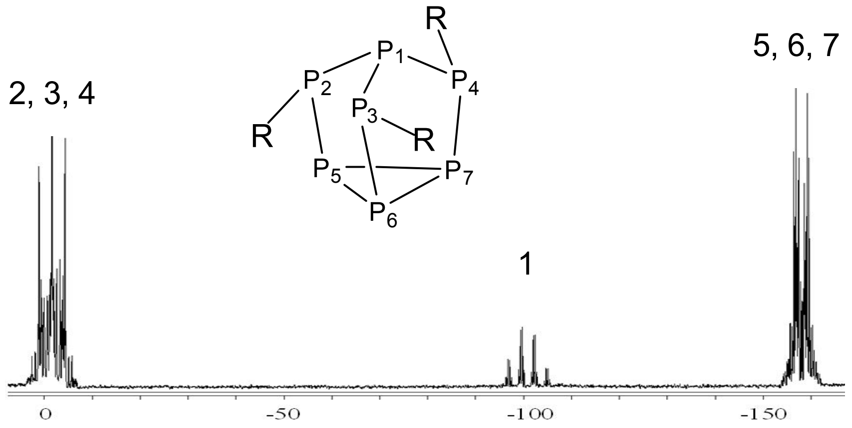


**Figure 1: $^{31}$P-NMR spectrum of $P_7(SiMe_3)_3$.**

During the NMR experiments, the quartet of the apical P-atom did not always display the correct intensity. Increasing the repetition time cured the problem, which obviously is caused by the slow relaxation of the apical P-atom. A measurement of the longitudinal relaxation time constant ($T_1$) for $P_7(SiMe_3)_3$ gave values 1.1±0.3 sec for the equatorial P-atoms, 9.2±1.5 sec for the apical P-atom and 2.7±0.3 sec for the basal P-atoms. It is necessary to wait about 50 sec (5T1) between the individual pulses, until full relaxation has occurred.

### 3.1.2 Isomerism of heptaphosphanes $P_7(SiR_3)_3$

The above-mentioned synthesis (Scheme 30) led to the isolation of the heptaphosphane $P_7(SiMe_3)_3$ which is known as a racemate of the chiral symmetric isomer. This was ascertained by $^{31}$P-NMR studies as well as by X-ray structure determination. This is easily understood, as the asymmetric isomer should be considerably higher in energy due to the steric interaction of two $SiMe_3$ groups. With smaller substituents such as H, Me or Et, a mixture of symmetric and asymmetric isomers generally is obtained. So far the isomers could not be separated by fractional crystallization. These results were also observed by Milyukov for the alkylheptaphosphane $P_7R_3$, alkyl groups R differing in bulkiness ($^n$Bu, $^nC_6H_{13}$, $^i$Bu, $^i$Pr, $CHEt_2$). [73] The analysis of the $^{31}$P-NMR spectrum revealed the ratios of the configurational isomers. [65]

To obtain some information on the energy differences between asymmetric and symmetric $P_7X_3$, ab initio HF/6-31G* and quantum chemical calculations for $P_7H_3$, $P_7Me_3$, $P_7(SiH_3)_3$ and $P_7(SiMe_3)_3$ were carried out. For tris(trimethylsilyl)heptaphosphane, DFT/B3LYP/6-31G* calculations were also performed for comparison with HF results, and the energy and structure of the transition state was calculated. Table 1 summarizes these results.

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[73] Milyukov, V. A.; Kataev, A. V.; Hey-Hawkins, E.; Sinyashin, O. G.; *Rus. Chem. B.* **2007**, 56(2), 304.

[65] Fritz, G.; Hoppe, K. D.; Hönle, W.; Weber, D.; Mujica, C.; Manriquez, V.; v. Schnering, H. G.; *J. Organomet. Chem.* **1983**, 249, 63.

**Table 1: Relative energies of symmetric and asymmetric $P_7X_3$ with X = H, Me, $SiH_3$ and $SiMe_3$**

| heptaphosphane | Method | isomer | $E_{rel}$ [$kJmol^{-1}$] |
|---|---|---|---|
| $P_7H_3$ | HF/6-31G* | sym | 0.3 |
| | | asym | 0.0 |
| $P_7Me_3$[a] | HF/6-31G* | sym | 0.0 |
| | | asym | 6.1 |
| $P_7(SiH_3)_3$[b] | HF/6-31G* | sym | 0.0 |
| | | asym | 13,5 |
| $P_7(SiMe_3)_3$ | HF/6-31G* | sym | 0.0 |
| | | asym | 39.0 |
| | | sym→asym transition state | 66.9 |
| | B3LYP/6-31G* | sym | 0.0 |
| | | asym | 32.3 |
| | | sym→asym transition state | 59.8 |

a): MINDO/3 calculations give a difference of 2.06 $kJmol^{-1}$;[106] b): The synthesis of $P_7(SiH_3)_3$ has been described briefly by G. Fritz, but quick decomposition even at -60°C occurs. [65]

As expected, the energy difference increases with the size of the substituents from ≈ 0 for $P_7H_3$ to about 30 – 40 $kJmol^{-1}$ for the trimethylsilyl group. The asymmetric → symmetric barrier is predicted to be about 27 $kJmol^{-1}$ which is considerably larger than RT for room temperature. Therefore, the asymmetric isomer of $P_7(SiMe_3)_3$ most likely is metastable and isolable.

The Figure 2 presents the structures of the stationary points at the B3LYP/6-31G* level of theory for $P_7(SiMe_3)_3$.

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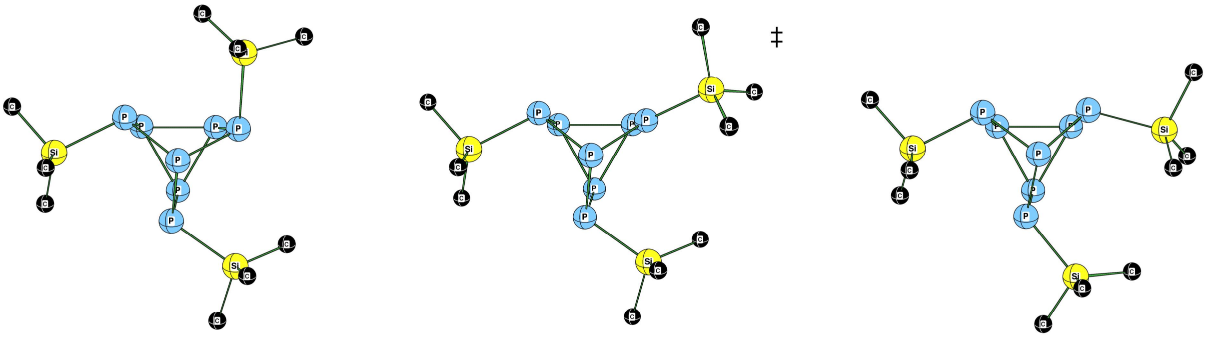
[106] Gleiter, R.; Böhm, M. C.; Eckert-Maksic, M. ; Schäfer, W.; Baudler, M.; Aktalay, Y.; Fritz, G.; Hoppe, K. D.; *Chem. Ber.* **1983**, 116, 2972.

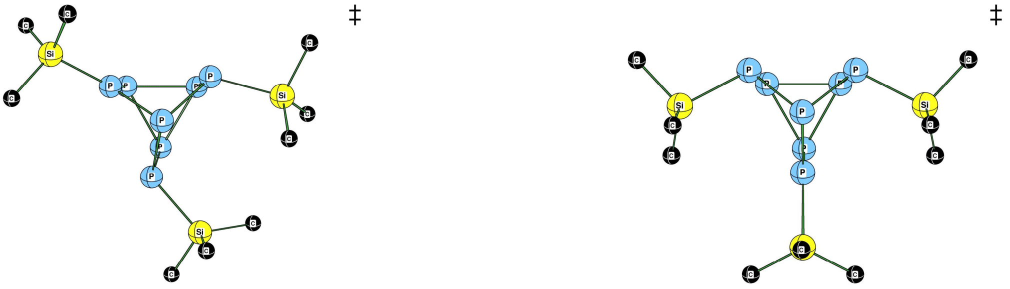
[65] Fritz, G.; Hoppe, K. D.; Hönle, W.; Weber, D.; Mujica, C.; Manriquez, V.; v. Schnering, H. G.; *J. Organomet. Chem.* **1983**, 249, 63.



$\Delta E_{rel}$ 0.0 kJmol$^{-1}$ $\Delta E_{rel}$ 59.7 kJmol$^{-1}$ $\Delta E_{rel}$ 31.7 kJmol$^{-1}$

**Figure 2: Top views of the calculated equilibrium structures of sym $P_7(SiMe_3)_3$ (left), asym $P_7(SiMe_3)_3$ (right) and of the sym Ÿ  asym transition state (middle).**

The asymmetric → asymmetric barrier is calculated as 32.0 kJmol$^{-1}$, with the structures of the transition states shown in Figure 3.



$\Delta E_{rel}$ 92.3 kJmol$^{-1}$ $\Delta E_{rel}$ 60.3 kJmol$^{-1}$

**Figure 3: Top view of the structure of the transition states for the asym-asym interconversion.**

## 3.2 Synthesis of heptaphosphanides

Metal polyphosphanides attract keen attention of researchers.

On the one hand, these compounds are intermediates in processes of elemental phosphorus transformation and studies of their structures and chemical properties allow deeper understanding of the mechanism of these reactions.

On the other hand, alkaline metal polyphosphanides containing phosphorus atoms in different oxidation states represent unique systems for the design of related complex polydentate molecules and clusters with potential practical significance. [107,70, 80]

Alkali metal salts of phosphorus-containing compounds continue to be of considerable interest because of their synthetic value as transfer reagents and the diversity of their solid-state structures. Among the variety of the alkali metal phosphanides, numerous binary metal polyphosphanides containing isolated Zintl species of the general formula $M_4P_6$, $M_3P_7$ and $M_3P_{11}$ have been established since the early seventies. However, only a very limited number of molecular alkali metal polyphosphanides with general formula $R_mP_nM_x$ have been caracterized structurally.

The development of new convenient methods for syntheses of alkaline metal polyphosphanides is an important and urgent task.

Only the polyphosphanides with isolated polycyclic anions of the types $R_nP_7^{(3-n)-}$ will be discussed in this thesis. Selection criteria are that the compounds are closely related to the organoheptaphosphanes and silylheptaphosphanes and that they can be prepared in solution.

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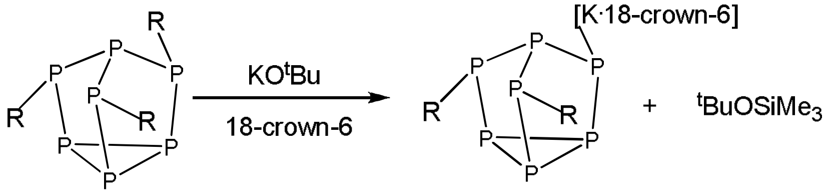
[107] v. Schnering, H. G. In *Rings, Chains, and Macromolecules of Main Group Elements*; (Rheingold, A. L., Ed.); Elsevier: Amsterdam, **1977.**

[70] v. Schnering, H. G.; *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 33.

[80] v. Schnering, H. G.; Hönle, W.; *Chem. Rev.* **1988**, 88, 243.

### 3.2.1 Synthesis of $[P_7(SiMe_3)_2]^-K^+$

The reaction of tris(trimethylsilyl)heptaphosphane $P_7(SiMe_3)_3$ with one equivalent $KO^tBu$ in presence of 18-crown-6 in toluene led to $[P_7(SiMe_3)_2]^-[K\cdot 18\text{-crown-6}]^+$ via the cleavage of one Si-P bond (Scheme 31)



**Scheme 31: Cleavage of one Si-P bond of $P_7(SiMe_3)_3$ using $KO^tBu$ (R=SiMe₃).**

Though the monoanion didn't crystallize from toluene and other solvents, the analysis of the $^{31}$P-NMR spectrum gave no doubt on the identity of the product. The spectrum consists of six second order resonances. The equatorial P-atoms bearing the $SiMe_3$-substituents give signals at -17.1 and -23.7 ppm, the equatorial P-atom carrying the negative charge gives a signal at -70.1 ppm. All three resonances are triplets with some fine structures. The apical P-atom which is bonded to the three equatorial phosphorus atoms gives a quartet at -88.7 ppm. The three basal P-atoms gives signal at -179.5 and -192.1 ppm.

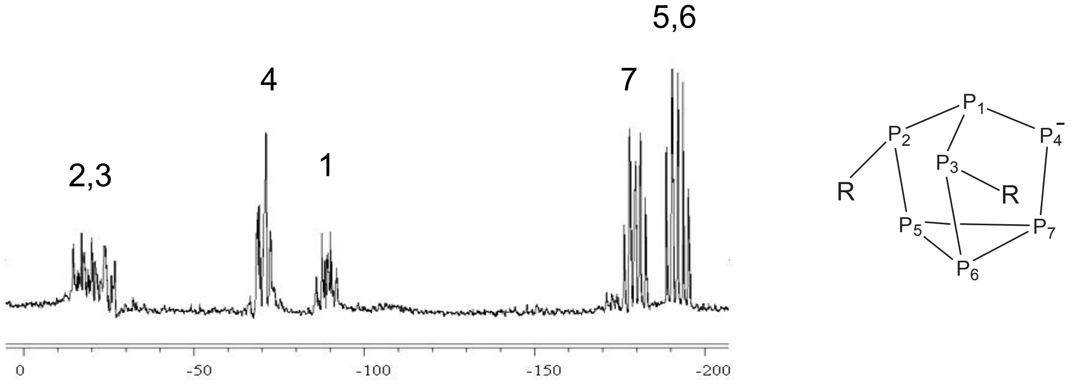
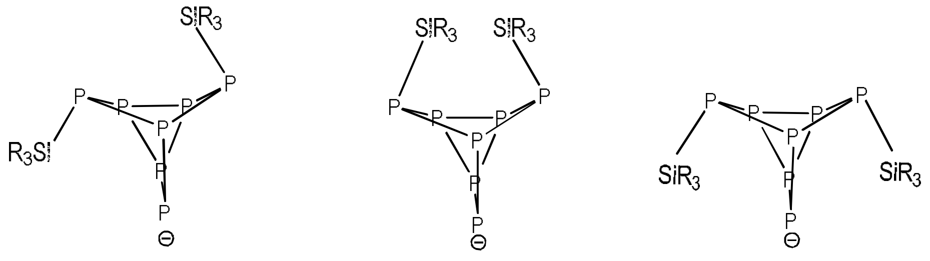


**Figure 4: $^{31}$P-NMR spectrum of $[P_7(SiMe_3)_2]^-[K\cdot 18\text{-crown-6}]^+$.**

The $^{31}$P-NMR spectrum contains six groups of signals which are in accordance with the presence of one isomer only in solution.

There are three possible isomers for $[P_7(SiMe_3)_2]^-$ as illustrated in Scheme 32. The structures **2** and **3** both have $C_s$ point symmetry with a mirror plane bisecting the $P_7$-cage. In both structures there are two pairs of equivalent phosphorus with the remaining three being unique. In structure **1**, all seven phosphorus atoms are inequivalent and seven resonances are expected. As the shifts of $P_5$ and $P_6$ are quite close to each other, they superimpose and only six groups of signals are observed. As the $^{31}$P-NMR data show only one isomer in solution, isomer **1** is expected to be in accordance with the observations.



**1** asymmetric (as) **2** symmetric (s1) **3** symmetric (s2)

**Scheme 32: Structure of the three isomers of heptaphosphanide $[P_7(SiR_3)_2]^-$.**

All the six resonances can be assigned in the $^{31}$P NMR spectrum through the use of the 2D $^{31}$P-$^{31}$P COSY NMR.

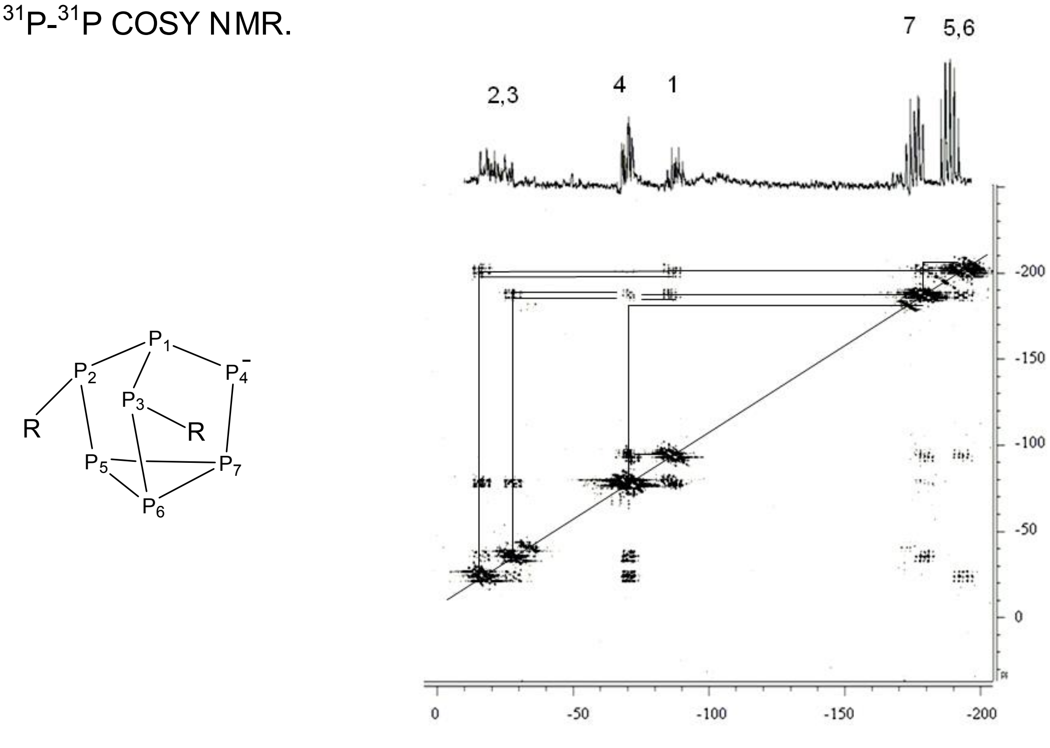
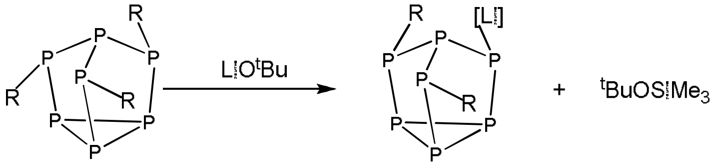


**Figure 5: $^{31}$P-COSY spectrum of $[P_7(SiMe_3)_2]^-[K\cdot 18\text{-crown-6}]^+$. The two-bond couplings are omitted for clarity.**

Noteworthy, the use of potassium greatly enhances the stability of the phosphanide anions in contrast to Li-heptaphosphanide such as $LiP_7(SiMe_3)_2$ which quickly decomposes.

### 3.2.2 Synthesis of $[P_7(SiMe_3)_2]^-Li^+$



**Scheme 33: Cleavage of one Si-P bond of $P_7(SiMe_3)_3$ using $LiO^tBu$ (R=$SiMe_3$)**

The reaction of $P_7(SiMe_3)_3$ with one equivalent $LiO^tBu$ in THF led to $[P_7(SiMe_3)_2]^-[Li]^+$. Quite surprisingly, an inversion at an equatorial P-atom occurred and the $C_s$ symmetric isomer **3** characterized by a mirror plan is formed.

In the spectrum the two equatorial P-atoms bearing the $SiMe_3$-substituent give a triplet with some fine structure at -33.7 ppm. The equatorial P-atom carrying the negative charge gives a resonance at -70.3 ppm (signal obscured by some small impurity). The signal of the apical P-atom is shifted to -58.8 ppm, about 30 ppm downfield from the corresponding resonance of isomer **1**. The signals of the three basal P-atoms are observed at -107.6 ppm (1P) and -174.1ppm (2P).

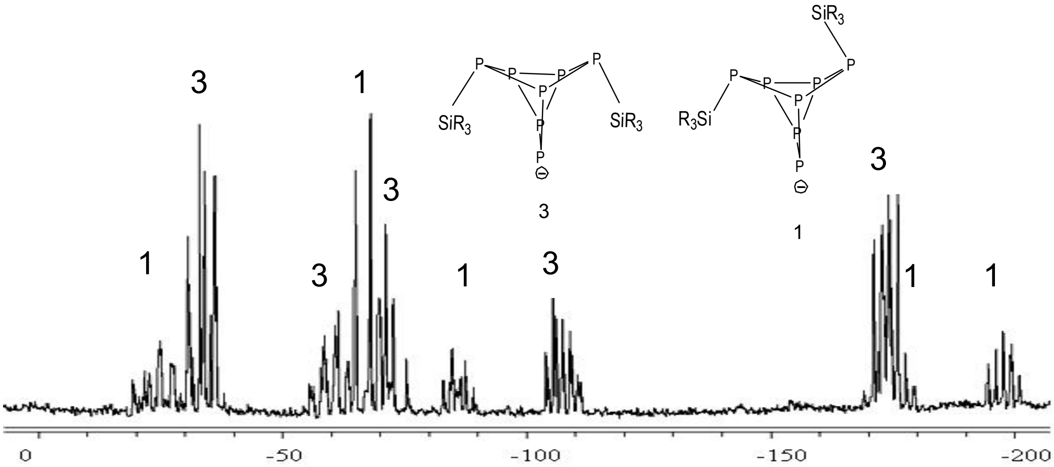


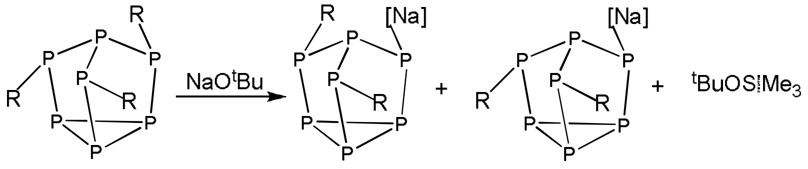
**Figure 6: $^{31}$P-NMR spectrum of $[P_7(SiMe_3)_2]^-[Li]^+$. Signals related to symmetric isomer 3 and asymmetric isomer 1 are marked.**

The presence of isomer **1** as well as **3** is consistent with the spectral features. On the basis of steric arguments and due to the size of the $SiMe_3$ substituent isomer **2** can be dismissed.

Interpretations of the $^{31}$P-NMR give approximately the ratio symmetric:asymmetric about 10:1, the solution contains predominantly the symmetric isomer **3**. A procedure to synthesize in quantitative yields the symmetric isomer could not be found, despite several attempts and by using different procedures. Some traces, roughly 10%, of the asymmetric isomer **1** were always present in the solution. Despite several attempts, crystals could not be obtained. A significant observation was that contrary to the observation of Fritz, [65] both the lithium and potassium salts were stable in solution for a couple of days.

The symmetric isomer of $[P_7(SiMe_3)_2]^-$ can be obtained from the asymmetric isomer only through inversion of a silyl-bearing P-atom, this process being characterized by a high energy barrier to activation of 66.2 kJ/mol. However the symmetric isomer has a lower energy because the system is sterically less strained. To further explore the relative stabilities of isomers **1** and **3**, quantum chemical B3LYP/6-31+G* calculations of equilibrium geometries for the naked anions as well as for the ion pairs $[P_7(SiMe_3)_2]^-K^+$ and $[P_7(SiMe_3)_2]^-Li^+$ were performed (Section 3.2.4).

### 3.2.3 Synthesis of $[P_7(SiMe_3)_2]^-Na^+$



**Scheme 34: Cleavage of one Si-P bond of $P_7(SiMe_3)_3$ using $NaO^tBu$ (R=$SiMe_3$)**

The reaction of tris(trimethylsilyl)heptaphospahne $P_7(SiMe_3)_3$ with one equivalent $NaO^tBu$ in THF led to $[P_7(SiMe_3)_2]^-[Na]^+$. As the $^{31}$P-NMR spectrum confirms, a mixture of the two isomers **1** and **3** with a ratio of about 1:1 was obtained (Figure 7). It was impossible to separate the anions by fractional crystallisation.

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[65] Fritz, G.; Hoppe, K. D.; Hönle, W.; Weber, D.; Mujica, C.; Manriquez, V.; v. Schnering, H. G.; *J. Organomet. Chem.* **1983**, 249, 63.

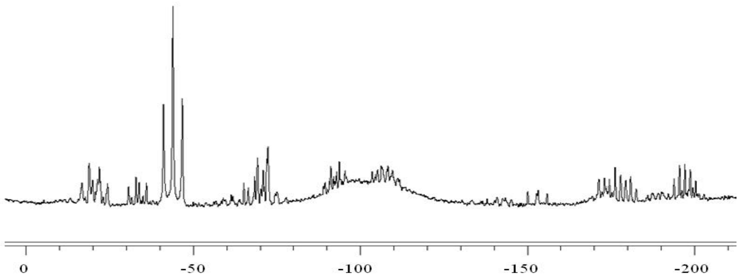


**Figure 7: $^{31}$P-NMR spectrum of $[P_7(SiMe_3)_2]^-[Na]^+$.**

### 3.2.4 Relative energies of the isomers of $[P_7(SiMe_3)_2]^-$

Figure 8 presents results for the naked anions. The symmetric isomer **3** represents the global minimum, separated by a barrier of about 65 kJmol$^{-1}$ from the asymmetric isomer **1** with a relative energy of +6.1 kJmol$^{-1}$. As expected, the phosphorus inversion barrier is almost the same as in $P_7(SiMe_3)_3$ (see Figure 1). Due to the interaction of the two trimethylsilyl groups, the relative energy of isomer **2** is about +50 kJmol$^{-1}$ which explains why its formation has never been observed. Therefore no further calculations for isomer **2** have been carried out.

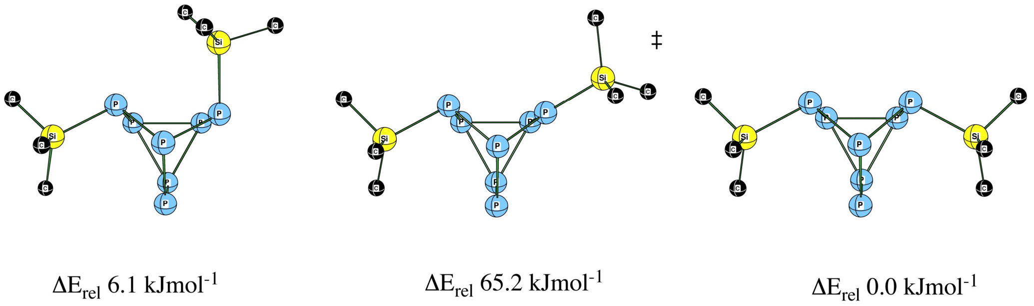
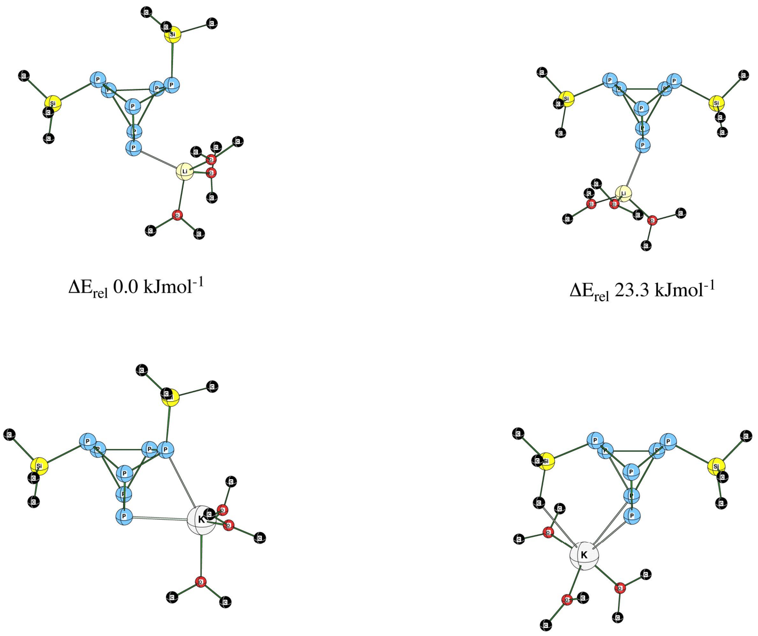


**Figure 8: Equilibrium geometries (H-atoms omitted) and relative energies for the isomers 1 and 3 of naked $[P_7(SiMe_3)_2]^-$ and for the transition state connecting 1 and 3.**

It turns out that the energy difference between **1** and **3** increases to about 25 – 30 kJmol$^{-1}$ when coordination of the cation to the $P_7$-cage is included, with **1** representing the minimum geometry now, irrespective of the nature of the cation. For these calculations, the presence of three molecules of dimethyl ether coordinating to $Li^+$ or $K^+$ has been assumed. Prior calculations have shown that dimethyl ether may serve as an excellent model for THF and can be used for speeding up the calculations without notable influence on the equilibrium geometries.

Figure 9 presents some selected results for the lithium as well as for the potassium salt. In all calculations, the lithium cation is predicted to coordinate to just one phosphorus atom, indicating a polar covalent bond. The potassium cation always has close contacts to at least two P-atoms, even if coordination to four dimethyl ether molecules is allowed.



$\Delta E_{rel}$ 0.0 kJmol$^{-1}$ $\Delta E_{rel}$ 23.3 kJmol$^{-1}$

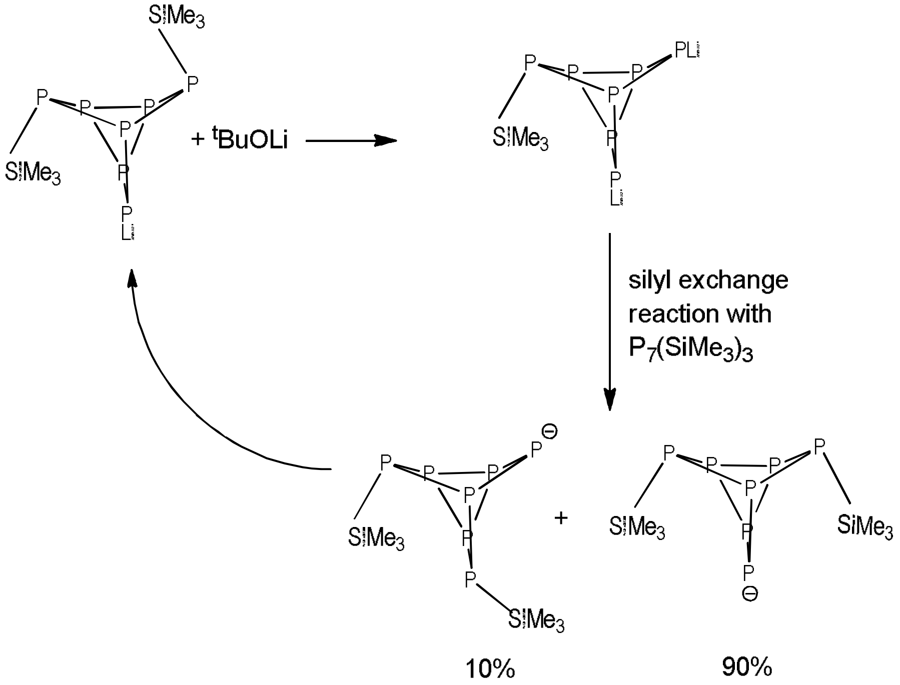
$\Delta E_{rel}$ 0.0 kJmol$^{-1}$ $\Delta E_{rel}$ 25.2 kJmol$^{-1}$

**Figure 9: Selected equilibrium geometries and relative energies for sym and asym $[P_7(SiMe_3)_2]^-$ $[Li(OMe_2)_3]^+$ and for sym and asym $[P_7(SiMe_3)_2]^-[K(OMe_2)_3]^+$. Hydrogen atoms on all methyl groups have been omitted for clarity.**

The calculations show that the lithium cation can also coordinate to a basal and to the apical P-atom in both isomers **1** and **3**. However, as the resulting geometries possess relative energies that are considerably larger (> ≈ 50 kJmol$^{-1}$), they have not been included in Figure 9 above. Similar results are obtained for the potassium salt. Here again, additional local minima differing in the position of the potassium cation and displaying high relative energies can be located.

The results of the quantum chemical calculations give no answer to the question why the symmetric isomer **1** forms in the reaction with LiO$^t$Bu and $^n$BuLi despite the large activation energy needed for phosphorus inversion.

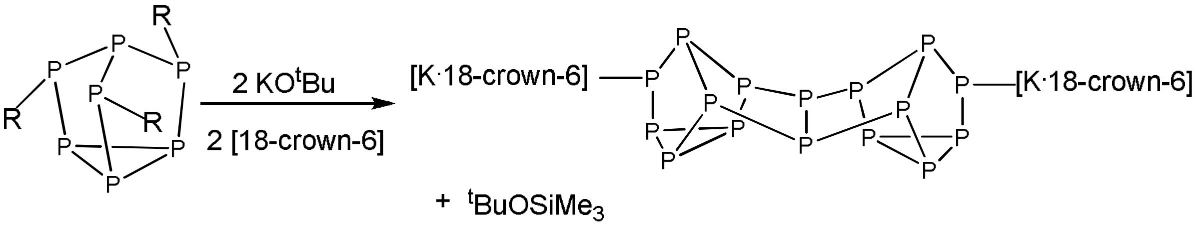
A possible reaction pathway might involve intermediate formation of $Me_3SiP_7Li_2$ in the first step, which then undergoes silyl exchange with $P_7(SiMe_3)_3$ to form isomer **3** of $LiP_7(SiMe_3)_2$ (Scheme 35). By this mechanism, phosphorus inversion can be avoided. The larger size of the potassium cation then can explain the exclusive formation of isomer **1** of $KP_7(SiMe_3)_2$. As seen from Figure 9, more space is available for $[K(OMe_2)_3]^+$ in the asymmetric isomer **1**.



**Scheme 35: Proposed rearrangement reaction leading to the symmetric isomer of $[P_7(SiMe_3)_2]^-$**

### 3.2.5 Synthesis of $[K^+]_2[P_{16}]^{2-}$

Surprisingly, the reaction of $P_7(SiMe_3)_3$ with two equivalents of KOᵗBu in presence of 18-crown-6 in toluene did not lead to $K_2[P_7(SiMe_3)]$ but to hexadecaphosphanide $K_2P_{16}$. Despite several attempts, using different reaction conditions (varying solvent and temperature) $[K^+]_2[P_7(SiMe_3)]^{2-}$ could not be synthsized. The yellowish solution quickly turned to a very dark reddish colour, typical for an anionic compounds. The hexadecaphosphide crystallized directly from the solution but crystals were to small and unsuitable for X-ray analysis. By-products such as $KP(SiMe_3)_2$ could be easily removed by decantation.



**Scheme 36: Reaction of $P_7(SiMe_3)_3$ with two equivalents of KO$^t$Bu (R=SiMe$_3$).**

The $^{31}$P-NMR spectrum below (Figure 10) shows six sets of signal at 60.2 ppm (4P), 39.7 ppm (2P), 6.9 (2P), -34.4 (2P) -133.2 (2P), -172.0 (4P). These shifts are in accordance with the literature data for $Li_2P_{16}$.

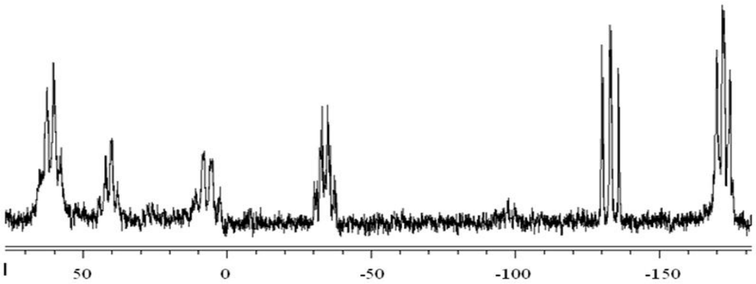


**Figure 10: $^{31}$P-NMR spectrum of $K_2P_{16}$ in toluene.**

Quite obviously, the dianion $[K^+]_2[P_7(SiMe_3)]^{2-}$ was not stable and quickly rearranges into $K_2P_{16}$.

As explained in chapter 2.3.2, $Li_2P_{16}$ is usually prepared in two steps. The first step consist in the transformation of $P_7(SiMe_3)_3$ to $P_7H_3$ by an alcohol HOR. The second step is the treatment of $P_7H_3$ by BuLi. We found that $K_2P_{16}$ can be synthesized in only one step by using an excess of KO$^t$Bu in toluene in presence of 18-crown-6 or without crown ether in a mixture toluene/DME (about 4:1).

In K. Hasslers group, V. Cappello synthesized $K_2P_7(SiMe(SiMe_3)_2]$ showing that it is possible to stabilize $K_2P_7R$ by increasing the size of the substituent.[108]

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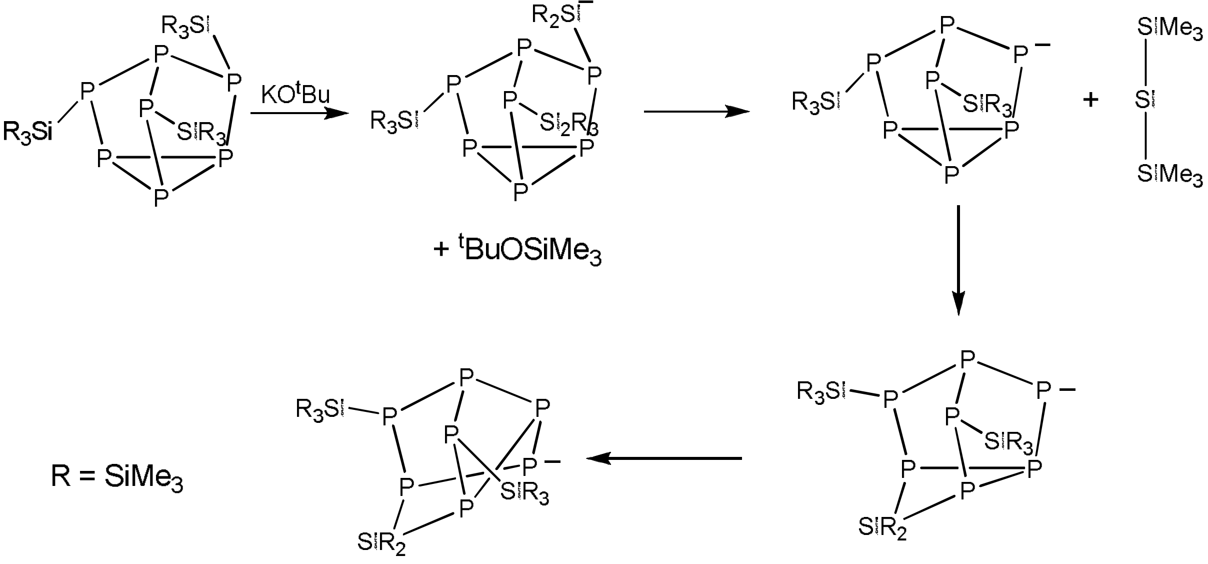
[108] Baumgartner, J.; Cappello, V.; Dransfeld, A.; Hassler, K.; „*Silicon Chemistry From the Atom to the Extended Systems*“ (Eds. P. Jutzi, U. Schubert), Wiley/VCH, Weinheim **2004**.

### 3.2.6 Synthesis of $[P_7(Si(SiMe_3)_3)_2]^-K^+$

*Synthesis from $P_7[Si(SiMe_3)_3]_3$:*

The reaction of $P_7[Si(SiMe_3)_3]_3$ with $KO^tBu$ in toluene proceeded in a way completely different from the reaction of $P_7(SiMe_3)_3$ with $KO^tBu$. Due to the bulkier hypersilyl groups, a SiSi-bond instead of a SiP-bond was cleaved initially, forming $^tBuOSiMe_3$ and a silyl anion which quickly rearranged into a phosphanide anion and bis(trimethylsilyl)silylene. The silylene then inserted into a PP-bond of the three membered ring of the $P_7$-cage forming $(SiR_2)P_7(SiR_3)_2$.[108] Thus, $P_7Hyp_2^-$ could not be prepared by this way.



**Scheme 37: Reaction of $P_7[Si(SiMe_3)_3]_3$ with one equivalent of $KO^tBu$ in toluene.**

*Synthesis from $(SiMe_3)P_7[Si(SiMe_3)_3]_2$:*

The heteroleptically substituted heptaphosphane $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ is a very interesting synthon in order to develop a practical synthetic method for $[P_7(Si(SiMe_3)_3)_2]^-K^+$. The silylated P-atoms bear two different silyl groups: the bulky hypersilyl $-Si(SiMe_3)_3$ and the less demanding $-SiMe_3$ group. The $P-SiMe_3$ bond should react faster than the two $P-Si(SiMe_3)_3$ bonds.

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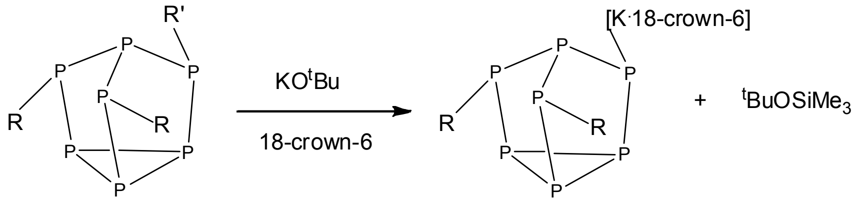
[108] Baumgartner, J.; Cappello, V.; Dransfeld, A.; Hassler, K.; „*Silicon Chemistry From the Atom to the Extended Systems*“ (Eds. P. Jutzi, U. Schubert), Wiley/VCH, Weinheim **2004**.

The action of KO$^t$Bu in toluene in presence of 18-crown-6 on $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ quantitatively led to $[P_7(Si(SiMe_3)_3)_2]^-K^+$. As expected the cleavage of the Si-P bond occured at the P-atom bearing the less space demanding $SiMe_3$ substituent. The reaction occured quite instantaneously at -50°C, the solution turning dark reddish several seconds after the addition of KO$^t$Bu.



**Scheme 38: Cleavage of the Si-P bond of $P_7[Si(SiMe_3)_3]_3$ with KO$^t$Bu. R= $Si(SiMe_3)_3$, R'= $SiMe_3$**

The formation of $[P_7(Si(SiMe_3)_3)_2]^-K^+$ was confirmed by the $^{31}$P-NMR spectrum as well as the $^{29}$Si-NMR spectrum. According to the NMR analysis no rearrangement in the structure of the $P_7$-cage was observed.

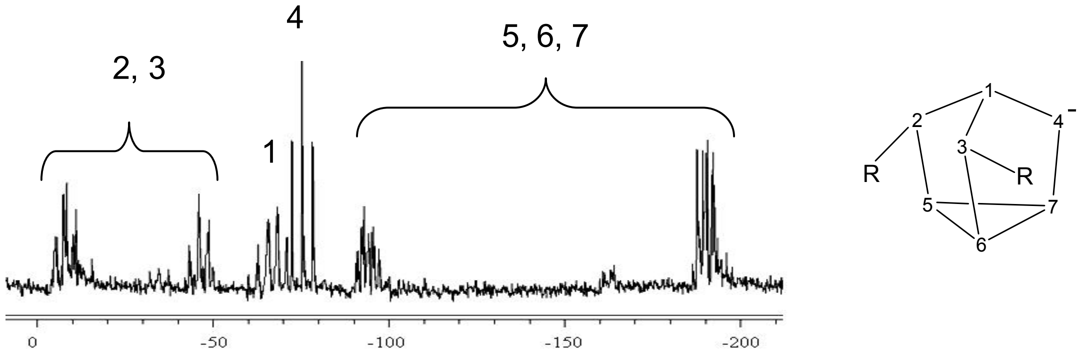


**Figure 11: $^{31}$P-NMR spectrum of $[P_7(Si(SiMe_3)_3)_2]^-K^+$ and structure of anion, the numbers replacing P-atoms. R= $Si(SiMe_3)_3$.**

The spectrum consists of six second order resonances with relative intensities 1:1:1:1:1:2. The equatorial P-atoms bearing the $Si(SiMe_3)_3$ substituents give signals at -9 (2) and -46 ppm (3). The equatorial P-atom carrying the negative charge gives a signal (triplet) at -75 ppm (4). The apical P-atom which is bonded to the three equatorial phosphorus atoms gives a quartet at -66 ppm (1). The basal P-atoms give signals at -94 and at -190 ppm (5, 6, 7). The six observed signals of relative intensity ratio 1:1:1:1:1:2 are in accordance with the formation of the asymmetric isomer. The anion was stable at room temperature for couple of days and for weeks if kept at -80°C. Crystals suitable for X-rays analysis could be grown from toluene at -80°C.

### 3.2.7 Crystal structure of $[P_7(Si(SiMe_3)_3)_2]^-K^+$

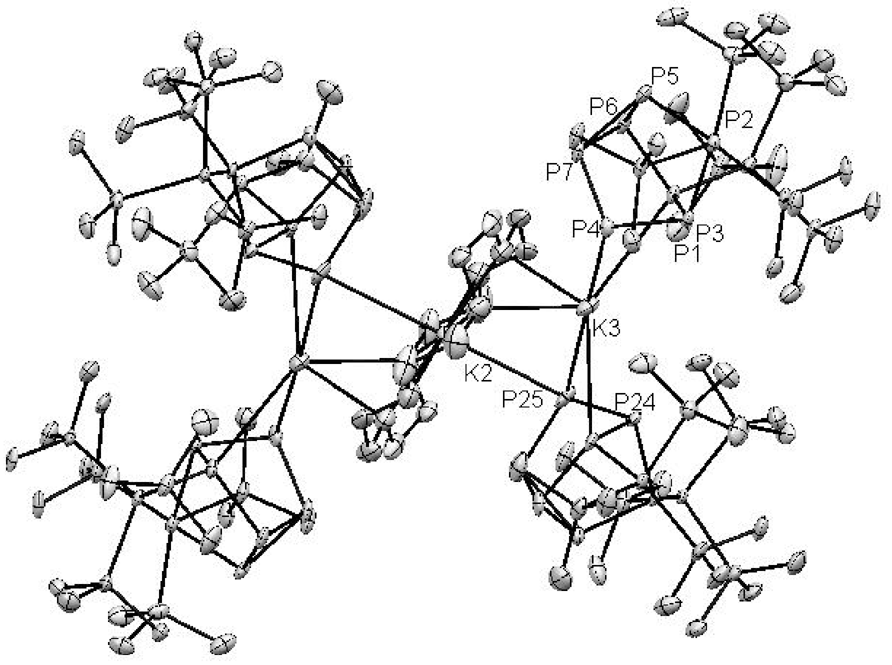
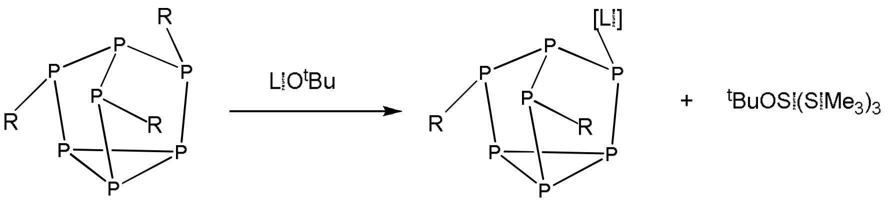


**Figure 12: ORTEP plot (30% probabilities) of the molecular structure of $[P_7(Si(SiMe_3)_3)_2][K\cdot18$-crown-6] and arrangement in the crystal. Important bond lenghts (Å) and bond angles (°) are: K2-P25: 3.5251(18); P4-K3: 3.360(2); P3-K3: 3.590(2); P24-K3: 3.4676(19); P25-K3: 3.476(2); P1-P4 : 2.1469(19); P2-P5: 2.1835(18); P2-P1: 2.1954(19); P3-P1: 2.185(2); P3-P6: 2.2066(19); P5-P6 : 2.232(2); P7-P4: 2.153(2); P7-P5: 2.221(2); P7-P6: 2.228(2); P1-P3-P6: 102.28(8); P5-P2-P1: 101.30(7); P4-P1-P3: 96.48(7); P4-P1-P2: 106.43(8); P3-P1-P2: 95.11(7); P4-P7-P5: 107.47(8); P4-P7-P6: 108.30(8); P5-P7-P6: 60.23(7); P2-P5-P7: 105.83(8); P2-P5-P6: 100.26(7); P3-P6-P7: 98.41(8); P3-P6-P5: 105.30(8); P1-P4-P7: 99.72(8).**

### 3.2.8 Synthesis of $[P_7(Si(SiMe_3)_3)_2]^-Li^+$

Quite surprisingly and in contrary to the reaction with $KO^tBu$, the reaction of $P_7[Si(SiMe_3)_3]_3$ with $LiO^tBu$ in THF led to $[P_7(Si(SiMe_3)_3)_2]^-Li^+$.



**Scheme 39: Cleavage of one Si-P bond of $P_7R_3$ using $LiO^tBu$. R= $Si(SiMe_3)_3$**

Despite the protection of the Si-P bond of the $Si(SiMe_3)_3$ groups observed for the reaction with $KO^tBu$, the reaction proceeded via the cleavage of one Si-P bond. This was obviously due to the smaller size of the Li atom. After a couple of days, no reaction was observed at room temperature, the complete reaction took place at 40°C during 10 days.

The $^{31}$P-NMR spectrum shows six signals with large intensities very similar to the spectrum of asymmetric $[P_7(Si(SiMe_3)_3)_2]^-K^+$ (see Section 3.2.5). The formation of the lithium salt $[P_7(Si(SiMe_3)_3)_2]^-Li^+$ occured without rearrangement in the $P_7$-backbone. In addition to the signals of asymmetric isomer (Figure 13), the presence of two other signals at -24 ppm ($P_2$= equatorial P-atoms bearing the $Si(SiMe_3)_3$ group) and -178 ppm ($P_7$= basal P-atom) could represent signals of the symmetric isomer **3**.

$[P_7(Si(SiMe_3)_3)_2]^-Li^+$ could also be obtained starting from $(SiMe_3)P_7[Si(SiMe_3)_3]_2$. The reaction took place instantaneously at -70°C, the solution turning reddish immediately. The presence of the symmetric isomer **3** in solution was more pronounced when starting from $(SiMe_3)P_7[Si(SiMe_3)_3]_2$. Crystal suitable for X-ray analysis could not be obtained.

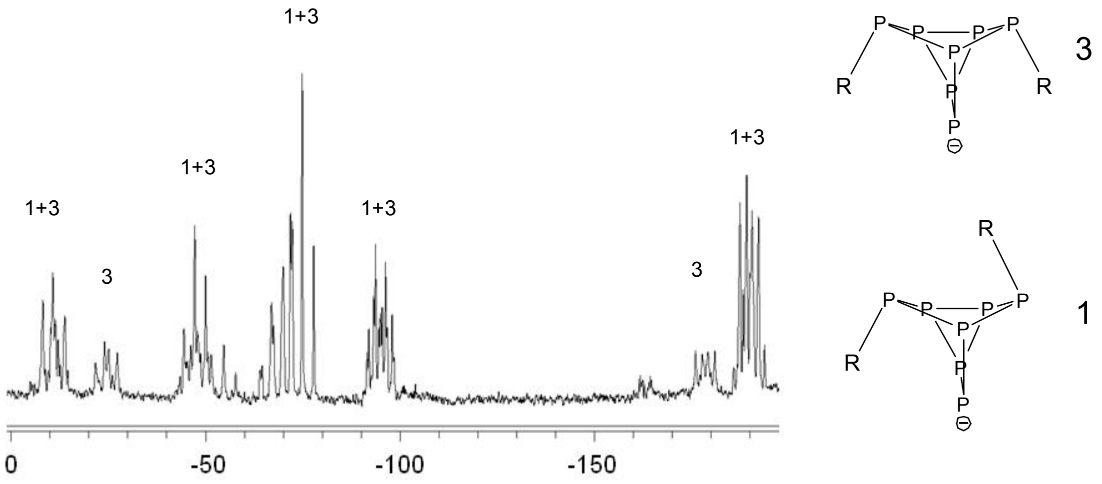
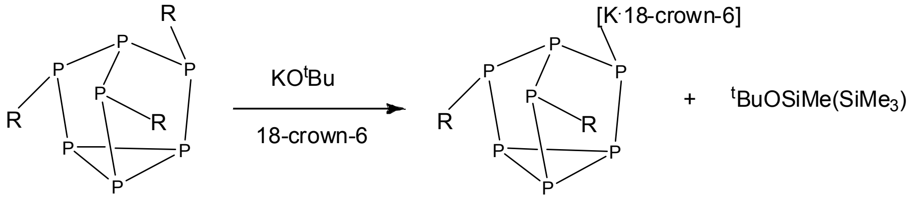


**Figure 13: $^{31}$P-NMR spectrum of $[P_7(Si(SiMe_3)_3)_2]^-Li^+$ and structure of the isomers present in solution with R= $Si(SiMe_3)_3$.**

### 3.2.9 Synthesis of $[P_7(SiMe(SiMe_3)_2)_2]^-K^+$



**Scheme 40: Cleavage of one Si-P bond of $P_7[(SiMe(SiMe_3)_2]_3$ using KO$^t$Bu. R= $SiMe(SiMe_3)_2$.**

The reaction of $P_7[SiMe(SiMe_3)_2]_3$ with KO$^t$Bu in toluene in presence of 18-crown-6 proceeded via the cleavage of a Si-P bond. No rearrangement in the structure of the $P_7$-cage was observed. The reaction occured quite instantaneously, the solution turning dark reddish immediately. Only five resonances with intensities 1:1:2:1:2 are observed because of overlapping of two signals between -50 ppm and -65 ppm ($P_3$ and $P_4$). The equatorial P-atom bearing the $SiMe(SiMe_3)_2$-substituent give signals at -18.9 and -58.9 ppm. The equatorial P-atom carrying the negative charge gives a signal (triplet) at -58.9 ppm. The apical P-atom which is bonded to the three equatorial phosphorus atoms gives a quartet at -36.3 ppm. The basal P-atoms give signals at -95.6 ppm and -190.4 ppm.

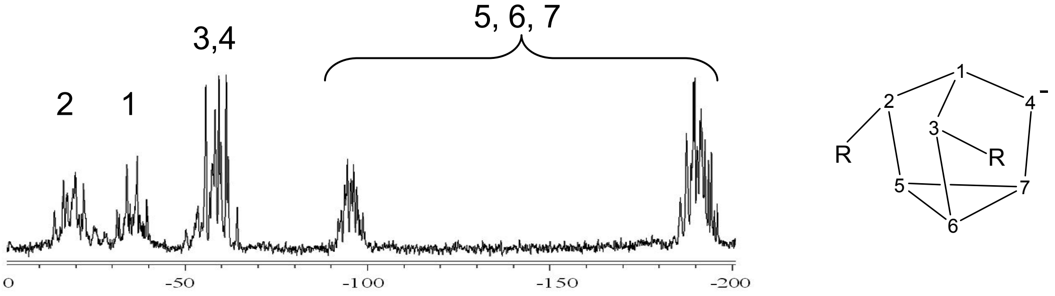


**Figure 14: $^{31}$P-NMR spectrum of $[P_7(SiMe(SiMe_3)_2)_2]^-K^+$ and structure of anion, the numbers replacing P-atoms. R= $SiMe(SiMe_3)_2$.**

The reaction occurred without change of symmetry with formation of the asymmetric isomer **1**. Due to substituent interactions, formation of the symmetric isomer was not observed. As the Si-P bond was less shielded than in $P_7[Si(SiMe_3)_3]_3$ due to the smaller size of the oligosilyl group, $P_7[SiMe(SiMe_3)_2]_3$ was expected to react more closely to $-SiMe_3$ than to $-Si(SiMe_3)_3$. The cleavage of a SiSi-bond instead of a SiP-bond was not observed according to the NMR analysis.

## 3.3 Derivatization of heptaphosphanide $[P_7(SiMe_3)_2]^-M^+$ (M=K, Li)

### 3.3.1 Attempts to bridge two $P_7$-cages

In the Zintl-phase $CsP_7$, chains of $P_7$-cages connected through PP-bonds are present. Interestingly, no neutral molecules composed of two or more interconnected $P_7$-cages are known at present, except $(SiMe_3)_2P_7P_7(SiMe_3)_2$ which was claimed to be a by-product of the reaction between $PCl_3$, $SiMe_3Cl$ and Mg.[99]

The anions $[P_7(SiMe_3)_2]^-M^+$ (M=K, Li) can be considered as good synthons for the synthesis of chains consisting of two or more $P_7$-cages connected by a PP-bond or by a spacer.

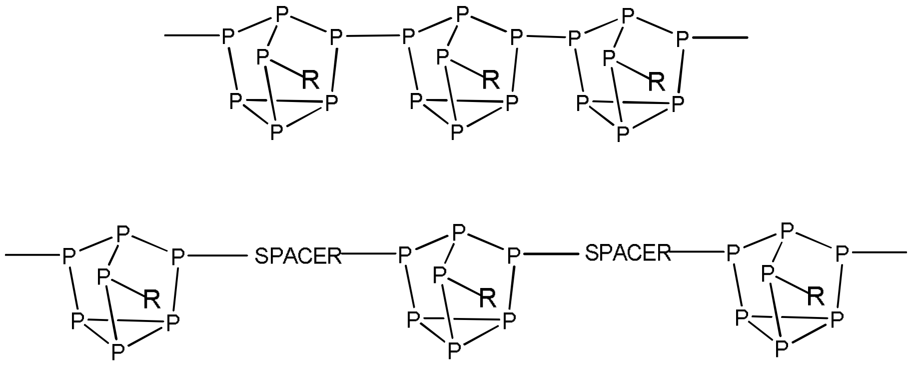


**Figure 15: Scheme of some target products consisting of chains of heptaphosphanes.**

A collection of synthetic strategies were used in this thesis, and the different attempts are summarized in Scheme 41. Many of these attempts were unsuccessful and led to unidentified products or simply to the degradation of the starting compound $MP_7R_2$. The main difficulties of these reactions are to keep the $P_7$-backbone unchanged.

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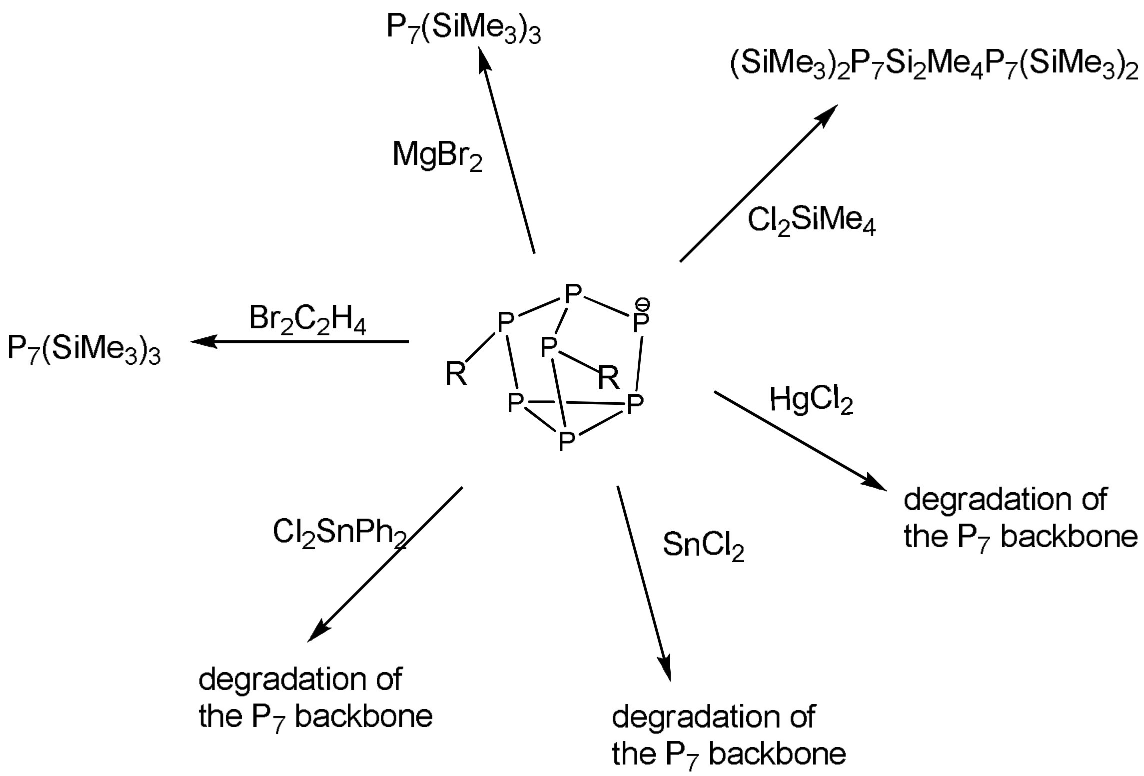
[99] Fritz, G.; Hölderich, W.; *Naturwiss.* **1975,** 62, 573.



**Scheme 41: Attempts to bridge two $P_7$-cages. R=$SiMe_3$.**

### 3.3.1.1 Reaction with $HgCl_2$

Starting from the results of Baudler who synthesized the diphosphane $(SiMe_3)_2P$-$P(SiMe_3)_2$ by reaction of $LiP(SiMe_3)_2$ with $HgCl_2$ (Section 2.2.1), this reaction pathway was applied to synthesize the target compound $(SiMe_3)_2P_7$-$P_7(SiMe_3)_2$. The potassium salt $[P_7(SiMe_3)_2]^-$ was first synthesised in a mixture of toluene and DME. Mercury (II) chloride $HgCl_2$ was then added to the mixture at low temperature. The decomposition of the $P_7$-cage occurred instantaneously, according to the $^{31}$P-NMR spectrum of the solution.

### 3.3.1.2 Reaction with $MgBr_2$

The target product of this reaction was $(SiMe_3)_2P_7$-Mg-$P_7(SiMe_3)_2$ consisting of two cages linked by a magnesium atom. Magnesium bromide $MgBr_2$ was added with a spatula to the solution of anions in a molar ration 1:2. The reddish solution turned dark yellow immediately, and a dark insoluble material settled on the bottom of the flask. A $^{31}$P-NMR spectrum was then recorded and showed the typical shifts of $P_7(SiMe_3)_3$.

### 3.3.1.3 Reaction with $BrCH_2CH_2Br$

In his dissertation V. Cappello reported on the formation of 1,2-di(hypersilyl)-1,2-bis(trimethylsilyl)diphosphane Hyp($SiMe_3$)P-P($SiMe_3$)Hyp by reaction of $BrCH_2CH_2Br$ on Hyp($SiMe_3$)PK at -80°C. The same procedure was followed starting from the potassium salt $[P_7(SiMe_3)_2]^-$. The reaction did not lead to $(SiMe_3)_2P_7$-$P_7(SiMe_3)_2$. The $^{31}$P-NMR spectrum displayed just the three signals typical for $P_7(SiMe_3)_3$ at 0, -100 and -150 ppm.

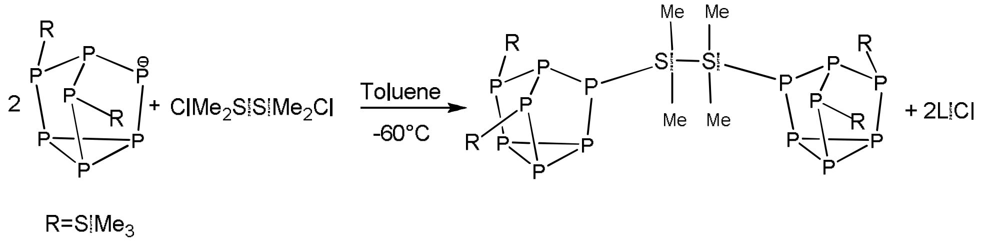
### 3.3.1.4 Reaction with $Cl_2SnPh_2$

In this attempt, two $P_7$-cages should be bridged by a tin atom with the final target compound $(SiMe_3)_2P_7$-$SnPh_2$-$P_7(SiMe_3)_2$. The lithium salt was first synthesised, and the diphenyltinchloride $Cl_2SnPh_2$ was added to the mixture at low temperature. A $^{31}$P-NMR measurement first showed the formation of several heptaphosphanes including the typical signals of $P_7(SiMe_3)_3$. The reaction was continued for 10 hours. The $^{31}$P-NMR analysis confirmed that the reaction led to the complete decomposition of the $P_7$-backbone.

### 3.3.1.5 Reaction with $SnCl_2$

The reaction of tin$^{(II)}$ chloride and $[P_7(SiMe_3)_2]^-$ was expected to give the compound $(SiMe_3)_2P_7$-Sn-$P_7(SiMe_3)_2$ which consists of two $P_7$-cages linked by a tin$^{(II)}$ atom. In a vial $[P_7(SiMe_3)_2]^-$ and $SnCl_2$ were brought together and toluene was added under stirring. Here again, the reaction led to the decomposition of the $P_7$-backbone.

### 3.3.1.6 Reaction with $Cl_2Si_2Me_4$



**Scheme 42: Synthesis of $(SiMe_3)_2P_7Si_2Me_4P_7(SiMe_3)_2$ starting from $[P_7(SiMe_3)_2]^-M^+$ and $Cl_2Si_2Me_4$**

The addition of $[P_7(SiMe_3)_2]^-M^+$ (M= K, Li) to a toluene solution of tetramethyldichlordisilane $Cl_2Si_2Me_4$ in a molar ratio 2:1 at very low temperature led to the compound $(SiMe_3)_2P_7Si_2Me_4P_7(SiMe_3)_2$. This compound which is composed of two $P_7$-cages connected by a disilane bridge formed in good yields. The $^{31}P$ NMR spectrum shown in Figure 16 displays six resonances in an intensity ratio 1:2:1:1:1:1, entirely consistent with the proposed structure. The signals at +25 and +5 ppm come from the equatorial (Si-substituted) P-atoms, the quartet at +5 originates from two overlapping triplets. As expected, the signal of the apical P-atom at -62 ppm is a quartet with some fine structure, and the three basal P-atoms give distinct signals at -146, -154 and -162 ppm. The compound crystallized well from hexane, but the crystals always were too small for X-ray diffraction experiment.

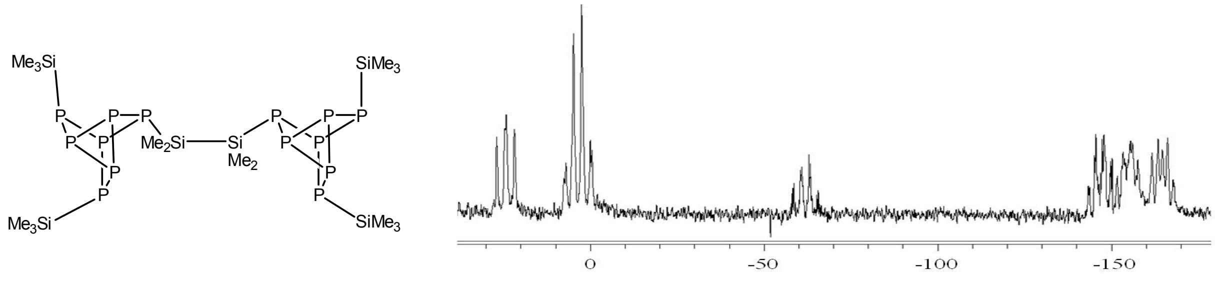
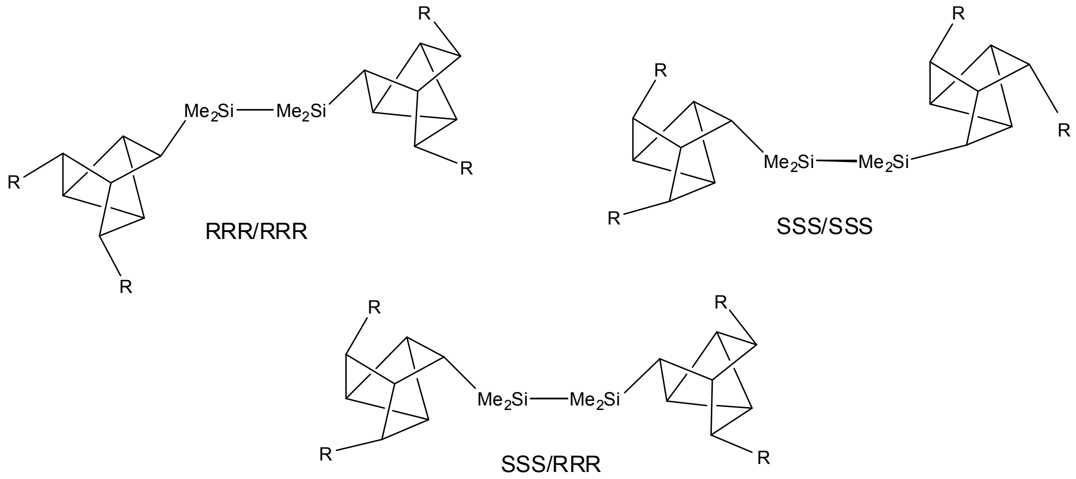


**Figure 16: $^{31}P$-NMR spectrum of $(SiMe_3)_2P_7Si_2Me_4P_7(SiMe_3)_2$ in toluene.**

The configuration of the three equatorial phosphorus atoms of a silylated sym derivative $P_7(SiR_3)_3$ can either be RRR or SSS. In principle and excluding high energy RRS and SSR configurations of the cages, $(SiMe_3)_2P_7(Si_2Me_4)P_7(SiMe_3)_2$ can exist as a mixture of three stereoisomers. A racemic modification (d, l enantiomers with configurations RRR/RRR and SSS/SSS) and a meso form with configuration RRR/SSS (Scheme 43).

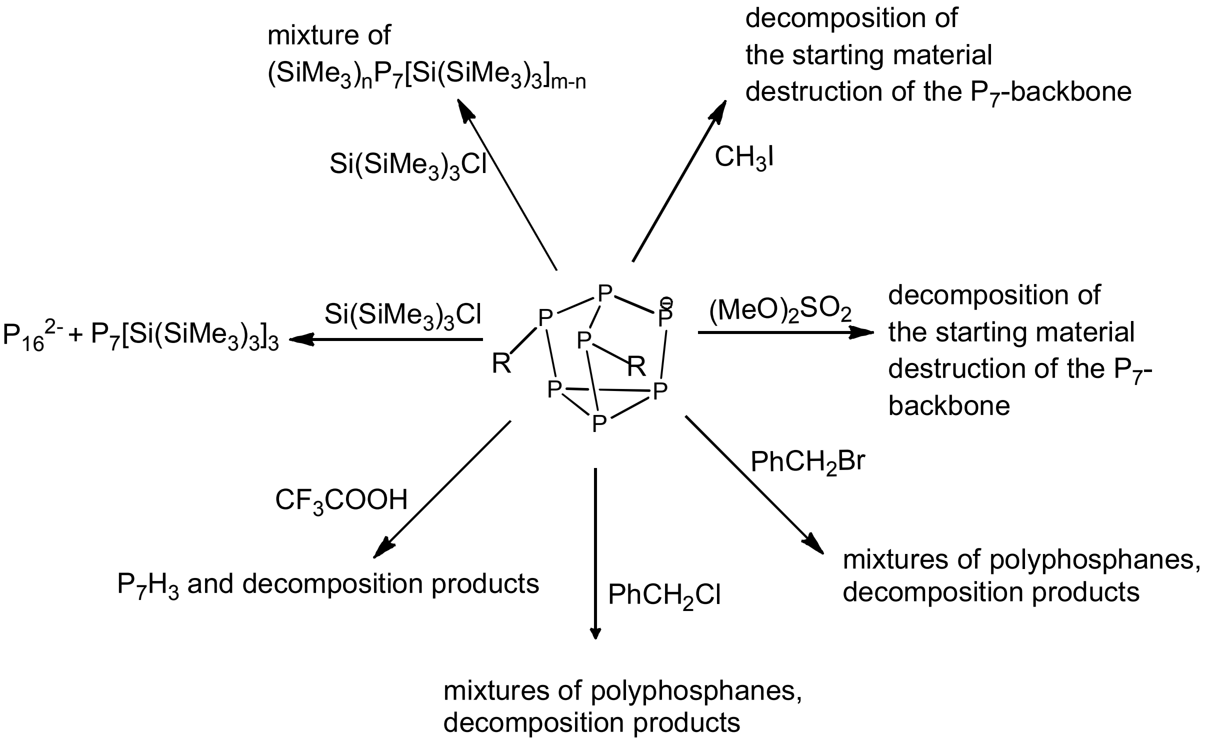
Furthermore, conformational isomerism due to hindered internal rotation around the SiSi-bond and both SiP-bonds of the central disilane bridge has to be considered. We anticipate that rotational isomerism is not important in NMR spectroscopy due to signal averaging. The $^{29}$Si and $^{31}$P-NMR spectra are consistent with either the presence of the d,l modification or the meso form, no indications for a meso/d,l mixture are detectable. For instance, just a single doublet is observed for the $SiMe_2SiMe_2$ group in the $^{29}$Si spectrum, and the $^1$H spectra display just two singlets in a ratio 3:1 for the $SiMe_3$ and $SiMe_2$ protons. However, the possibility that all signals of meso and d,l are so close together that they superimpose and cannot be resolved with NMR spectroscopy cannot be excluded.



**Scheme 43: Possible configurations for $(SiMe_3)_2P_7Si_2Me_4P_7(SiMe_3)_2$.**

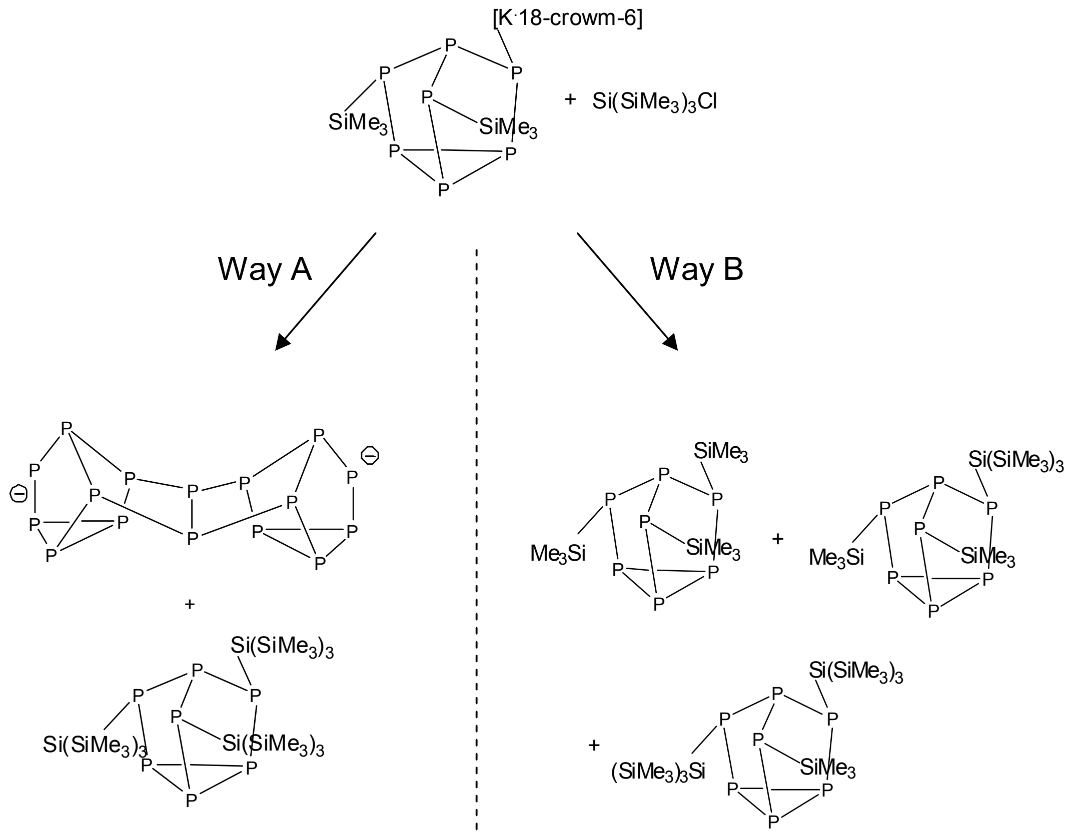
### 3.3.2 Attempts to synthesize heteroleptic heptaphosphanes

One of the goals of this work is the synthesis of novel heteroleptic cages of the type $P_7R_2R'$ where R is silyl-group and R' a silyl- or organo-group. Many of compounds of the type $R_3P_7$ are formed usually from the reactions of halogenosilanes with alkali metal phosphanides $M_3P_7$ (see Section 2). Starting from these results, heptaphosphanides of the type $MP_7R_2$ (M=K, Li) appear in fact as good syntons for the synthesis of heteroleptic heptaphosphanes $P_7R_2R'$. The different attempts are summarized in Scheme 44 below.



**Scheme 44: Attempts to synthesize heteroleptically substituted heptaphosphanes $P_7R_2R$ô R=$SiMe_3$**

### 3.3.2.1 Reaction with $Si(SiMe_3)_3Cl$



**Scheme 45: Reaction between $M^+[P_7(SiMe_3)_2]^-$ and $ClSi(SiMe_3)_3$ A: $ClSi(SiMe_3)_3$ was added dropwise to anion ï B: The anion was added dropwise to $ClSi(SiMe_3)_3$.**

In order to synthesize the heptaphosphane $[(SiMe_3)_3Si]P_7(SiMe_3)_2$, the "salt elimination" pathway consisting of addition of $ClSi(SiMe_3)_3$ to $M^+[P_7(SiMe_3)_2]^-$ was investigated (Scheme 45).

The reaction of $KP_7(SiMe_3)_2$ or $LiP_7(SiMe_3)_2$ with $ClSi(SiMe_3)_3$ could be performed under conditions which preserved the $P_7$-backbone. But despite several attempts the target compound $Si(SiMe_3)_3P_7(SiMe_3)_2$ could not be synthesized. By addition of a toluene solution of $ClSi(SiMe_3)_3$ to $KP_7(SiMe_3)_2$ or $LiP_7(SiMe_3)_2$, a solution typical of a neutral heptaphosphane was obtained and dark crystals precipitated on the wall of the flask (way A). Surprisingly, the presence in solution of only $[Si(SiMe_3)_3]_3P_7$ was confirmed by the NMR analysis. The $^{31}P$-NMR spectrum and the $^{29}Si$-NMR spectrum displayed signals which were consistent with the literature and gave no doubt on the identity of the product. Quite obviously a substituent exchange reaction between $-SiMe_3$ and $-Si(SiMe_3)_3$ had occured. The signals of monophosphanes $P(SiMe_3)_3$ at

-245 ppm and $Si(SiMe_3)_3P(Sime_3)_2$ at -268 ppm were also observed. The crystals were dissolved in THF, and a NMR analysis showed the presence of the dianion $[P_{16}]^{2-}$ with six sets of signal at 60.2 ppm (4P), 39.7 ppm (2P), 6.9 (2P), -34.4 (2P), -133.2 (2P), -172.0 (4P). The formation of $[P_{16}]^{2-}$ was also observed by Milyukov in the reaction of $Na_3P_7$ with aryltosylate and cyclohexyltosylate. [73]

A substituent exchange could not be avoided when the solution of anion was added to the solution of HypCl at low temperature (way B). The $^{31}$P-NMR spectrum displays more than the three triplets for the equatorial P-atoms that are expected for $[(SiMe_3)_3Si]P_7(SiMe_3)_2$, and the signal in the region of the apical P-atom (-100 ppm) consists of three overlapping quartets, each with some fine structure (Figure 17). In the reaction mixture, the two main products were $[(SiMe_3)_3Si]P_7(SiMe_3)_2$ and $[(SiMe_3)_3Si]_2P_7(SiMe_3)$. Signals of $P_7(SiMe_3)_3$ and $[(SiMe_3)_3Si]_3P_7$ are very weak in the spectrum below.

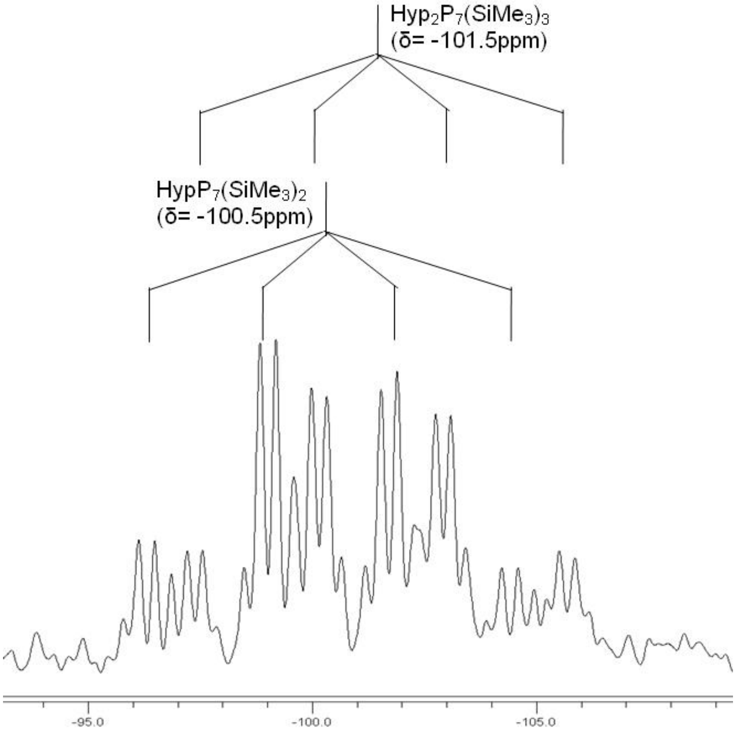


**Figure 17: Expansion of the $^{31}$P-NMR spectrum of the solution of a mixture of $Hyp_nP_7(SiMe_3)_{3-n}$ (n = 0, 1, 2, 3) in the range -90 to -110ppm. Hyp= $Si(SiMe_3)_3$.**

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[73] Milyukov, V. A.; Kataev, A. V.; Hey-Hawkins, E.; Sinyashin, O. G.; *Rus. Chem. B.* **2007**, 56(2), 298.

### 3.3.2.2 Reaction with $PhCH_2Br$, $PhCH_2Cl$

In order to synthesize the compound $PhCH_2P_7(SiMe_3)_2$ a solution of $LiP_7(SiMe_3)_2$ was added dropwise to a toluene solution of benzyl bromide at low temperature. No change of the colour of the reddish solution could be observed ever after stirring for 10 days at room temperature. The $^{31}$P-NMR spectrum displayed too many signals to allow the identification of products present in solution. The signals of the anion were however identified. It was impossible to separate any compound present in the mixture by fractional crystallisation. The same result was obtained with benzyl chloride.

### 3.3.2.3 Reaction with $(CH_3O)_2SO_2$

Dimethylsulfate is used as methylating agent in chemistry. Using $Me_2SO_4$ the anion $M^+P_7(SiMe_3)_2^-$ should be methylated forming $MeP_7(SiMe_3)_2$. According to the $^{31}$P-NMR the addition of a toluene solution of $Me_2SO_4$ to the anion $P_7(SiMe_3)_2^-$ rapidly led to the complete degradation of the $P_7$-backbone.

### 3.3.2.4 Reaction with $CH_3I$

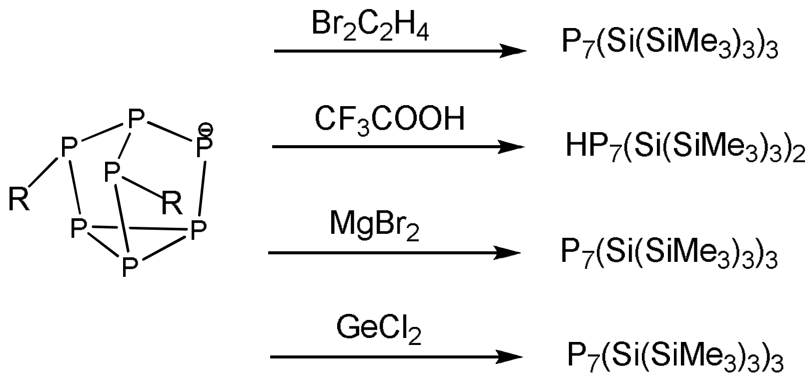
Iodomethane as a methylation reagent was used for the attempted synthesis of $MeP_7(SiMe_3)_2$. The anion was added to the iodomethane dissolved in toluene at low temperature. Although salts settled on the bottom of the flask, the NMR analysis confirmed just the complete destruction of the $P_7$-backbone.

### 3.3.2.5 Reaction with $CF_3CO_2H$

Trifluoroacetic acid was used in this attempt to protonate the anion $M^+P_7(SiMe_3)_2^-$. The anion was first synthesized and $CF_3CO_2H$ was added with a syringe at low temperature. The reddish solution instantaneously turned yellowish. A $^{31}$P-NMR spectrum showed no signal. Yellowish insoluble products settled on the bottom of the flask which could not be characterized further.

## 3.4 Derivatization of $[P_7(Si(SiMe_3)_3)_2]^-M^+$ (M=K, Li)

Due to the size of the -$Si(SiMe_3)_3$ group, the anion $[P_7(Si(SiMe_3)_3)_2]^-$ could react in a different way than $[P_7(SiMe_3)_2]^-$. The hypersilyl group was expected to stabilize the $P_7$-backbone and to offer the possibility of successful synthesis of heptaphosphanes $RP_7[Si(SiMe_3)_3]_2$ and chains of $P_7$-cages. Several attempts are summarized in Scheme 46.



**Scheme 46: Results of attempted synthesis of heteroleptically substituted heptaphosphanes $P_7R_2$Rôand chains of $P_7$-cages. R= $Si(SiMe_3)_3$.**

### 3.4.1.1 Reaction with $MgBrEt_2O$

In order to synthesize the compound $[R_2P_7]^-$-$Mg^{2+}$-$[P_7R_2]^-$, the reaction between $MgBr_2$ and $[P_7(Si(SiMe_3)_3)_2]^-$ was investigated. The potassium anion was synthesized, and magnesium bromide $MgBrEt_2O$ was added under vigorous stirring. A reaction occured as the solution turned dark immediately but did not lead to the attempted product. Quite surprisingly the NMR spectrum showed the signals of $P_7(Si(SiMe_3)_3)_3$.

### 3.4.1.2 Reaction with $BrCH_2CH_2Br$

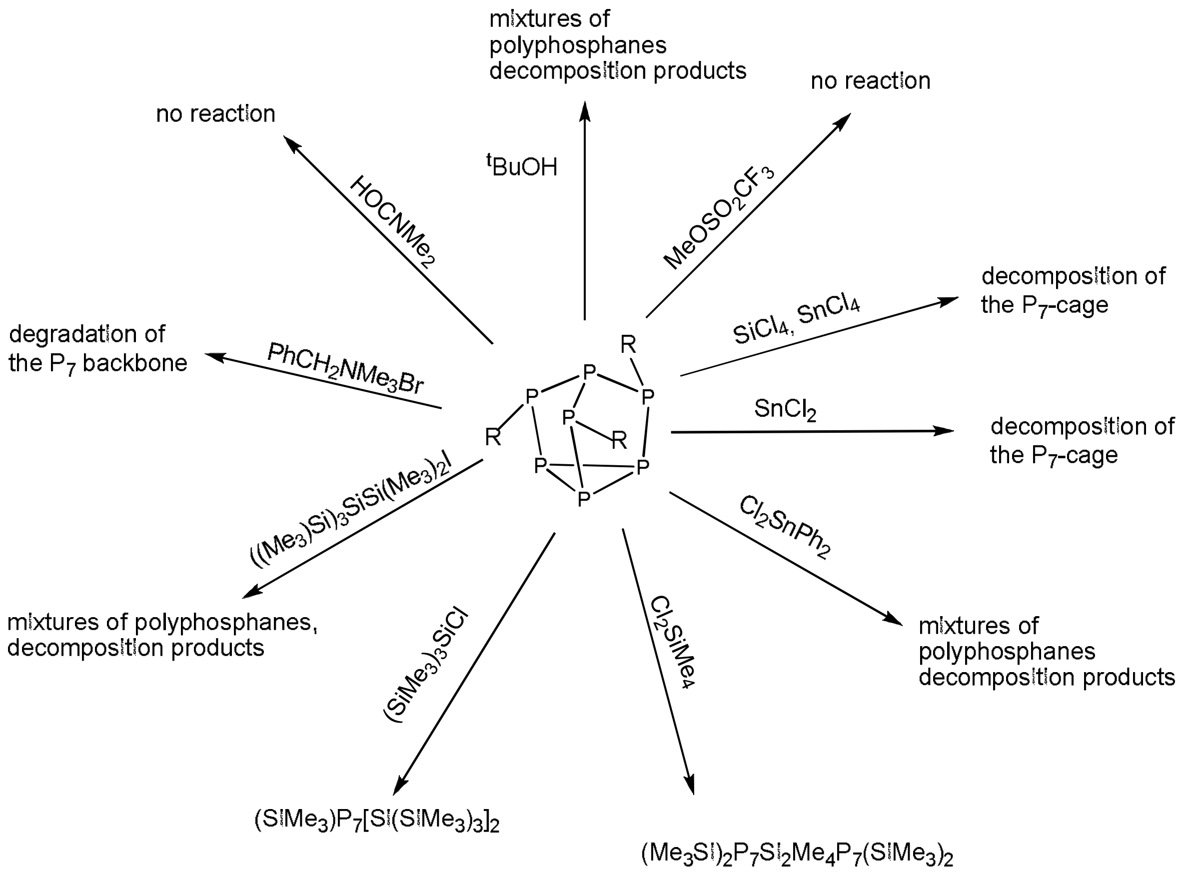
For this reaction, the lithium anion was synthesized and a toluene solution of dibromoethane was added dropwise at low temperature. We anticipated that the reaction would lead to the target product $Si(SiMe_3)_3)_2P_7$-$P_7Si(SiMe_3)_3)_2$. As observed for the reaction of $[P_7(SiMe_3)_2]^-$ and $Br_2C_2H_4$, after some unclear rearrangements and obvious silyl exchange reaction, the solution contained only $P_7(Si(SiMe_3)_3)_3$. The $^{31}$P-NMR spectrum displayed three sets of signals at -1,9 ppm (m, 3P), -100,8 ppm (m, 1P), -165,6 ppm (m, 3P).

#### 3.4.1.3 Reaction with $GeCl_2$

In this case, use of germanium dichloride should allow the synthesis of $Si(SiMe_3)_3)_2P_7$-Ge-$P_7Si(SiMe_3)_3)_2$. A toluene solution of $GeCl_2$ was added dropwise at low temperature to a toluene solution of the potassium salt $[P_7(SiMe_3)_2]^-$. The $^{31}$P-NMR analysis confirmed just the formation of $P_7(Si(SiMe_3)_3)_3$.

## 3.5 Derivatization of tris(trimethylsilyl)heptaphosphane $P_7(SiMe_3)_3$

As explained in the Section 2.1.3, the trimethylsilyl substituent $SiMe_3$ is known as a very good leaving group. Therefore, tris(trimethylsilyl)heptaphosphane $P_7(SiMe_3)_3$ should be a suitable starting material for the synthesis of other heptaphosphanes and chains of $P_7$-cages connected by PP-bonds or spacers. The different attempts, successful and unsuccessful, are summarised in Scheme 47 below.



**Scheme 47: Attempts to functionalize tris(trimethylsilyl)heptaphosphane $P_7(SiMe_3)_3$.**

### 3.5.1 Reaction with $MeOSO_2CF_3$

Methyl trifluoromethanesulfonate (methyl triflate) is a very powerful methylating reagent, and the reaction with $P_7(SiMe_3)_3$ was expected to afford $MeP_7(SiMe_3)_2$, besides $SiMe_4$. MeOTf was added to a solution of $P_7(SiMe_3)_3$ at very low temperature. Despite the polarity of the Si-P bond and the use of this very powerful methylating agent, no reaction was observed according to the $^{31}$P-NMR analysis, even after a couple of weeks.

### 3.5.2 Reaction with $HCON(CH_3)_2$ (DMF)

Dimethylformamid was used in this reaction as reactant to obtain the target product $[(Me)_2NH]CP_7(SiMe_3)$. DMF and $P_7(SiMe_3)_3$ were first mixed in a molar ratio 1:1 in dry toluene, and the mixture was stirred for a couple of days. No reaction occured according to the $^{31}$P-NMR spectrum. A large excess (1:100) was then added to the toluene solution. Even with this excess no reaction could be observed.

### 3.5.3 Reaction with benzyltrimethylammonium bromide $[PhCH_2NMe_3]^+Br^-$

Benzyltrimethylammonium bromide can be used as an effective halogenating and oxidizing agent in synthetic chemistry. The action of $PhCH_2NMe_3Br$ on $P_7(SiMe_3)_3$ was expected to give the heptaphosphane $PhCH_2P_7(SiMe_3)_2$ via cleavage of one P-Si bond. $PhCH_2NMe_3Br$ was added to a THF solution of $P_7(SiMe_3)_3$ and the solution was stirred for 8 days. Initially, a rearrangement of the $P_7$-backbone was observed but the reaction finally led to the degradation of the cage.

### 3.5.4 Reaction with $SnCl_2$

In this attempt, the target product was $(SiMe_3)_2P_7$-Sn-$P_7(SiMe_3)_2$ which consist of two neutral cages linked by a tin atom. Tin dichloride was added to a toluene solution of $P_7TMS_3$ a low temperature. According to the $^{31}$P-NMR spectrum, the reaction led to the destruction of the cage.

### 3.5.5 Reaction with $Cl_2SnPh_2$

The target product of this reaction was $(SiMe_3)_2P_7$-$SnPh_2$-$P_7(SiMe_3)_2$ which consist of two $P_7$-cages linked by a diphenyl tin bridge. $P_7(SiMe_3)_3$ and $Cl_2SnPh_2$ were brought together and dry DME was added dropwise to the mixture at low temperature. A reaction occurred, but the product could not be identified with reliability. The signals observed in the $^{31}P$-NMR spectrum could match with the formation of $(SiMe_3)_2P_7P_7(SiMe_3)_2$ or $(SiMe_3)_2P_7SnPhCl$.

## 3.6 Derivatization of $P_7(SiR_3)_3$ by silyl exchange

Reactions of silylated heptaphosphanes $P_7(SiR_3)_3$ by cleavage of Si-P bonds are complicated because rearrangement with destruction of the $P_7$-backbone and formation of many by-products often occur. In addition to cleavage of Si-P bonds of $P_7(SiMe_3)_3$, cleavage of P-P bonds is also possible. Derivatization of $P_7(SiMe_3)_3$ without degradation of the $P_7$-backbone turns out to be very difficult.

For example, $P_7(SiMe_3)_3$ reacted with iodine under formation of $P_2I_4$, $PI_3$, $Me_3SiI$ and insoluble polymeric products. These compounds were also produced when iodine is used in a low molar ratio (1:0.5). Reaction with $Me_2PCl$ and $MePCl_2$ also led to destruction of the $P_7$ cage. $C_6F_5Br$ gave $P(C_6F_5)_3$ and polymeric substances, and $CH_2Cl_2$ or $C_6H_5Br$ did not react at all. [65]

In 1986, H.G von Schnering synthesised new derivatives $P_7(MPh_3)_3$ (M = Si, Ge, Sn) by reaction of tris(trimethylsilyl)heptaphosphane $P_7(SiMe_3)_3$ with compounds $ClMPh_3$. The substitution of $MMe_3$ by $MPh_3$ occurred only in a carefully chosen solvent, in which $P_7(MPh_3)_3$ had a very low solubility. [100] An example is the reaction of $P_7(SiMe_3)_3$ with $ClSiPh_3$ which gave $P_7(SiPh_3)_3$. In toluene both products have a good solubility and $P_7(SiPh_3)_3$ was formed only in very low yield. In DME, the reaction was quantitative and led to $P_7(SiPh_3)_3$, which is not soluble. The driving force of the reaction was the lower solubility of the $P_7(MPh_3)_3$ compounds.

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[65] Fritz, G.; Hoppe, K. D.; Hönle, W.; Weber, D.; Mujica, C.; Manriquez, V.; v. Schnering, H. G.; *J. Organomet. Chem.* **1983**, 249, 63.

[100] Mujica, C.; Weber, D.; v. Schnering, H. G.; *Z. Naturforsch.* **1986**, 41B, 991.

### 3.6.1 Reaction with $(Me_3Si)_3SiSiMe_2I$

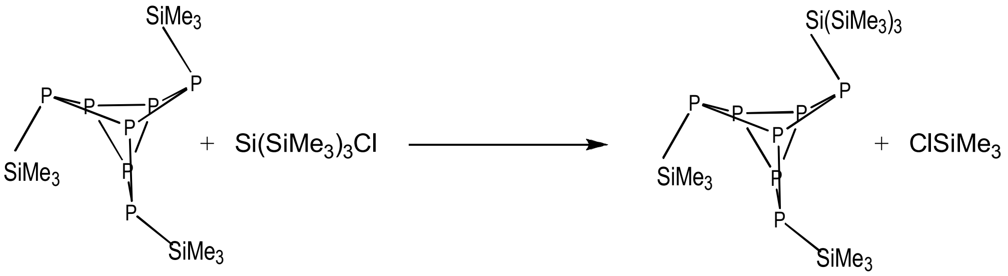
The target product of the reaction of $(Me_3Si)_3SiSiMe_2I$ with $P_7(SiMe_3)_3$ was $[(Me_3Si)_3SiMe_2Si]P_7(SiMe_3)_2$. The reagents were brought together and DME was added dropwise at -50°C. After a couple of days, a reaction occurred but we were not able to identify by NMR-analysis all the compounds present in solution. It was impossible to separate any pure compound from the mixture by fractional crystallisation. Obviously more than one Si-P bond had reacted and a rearrangement in the $P_7$ structure had occured.

### 3.6.2 Reaction with $SiCl_4$ and $SnCl_4$

The reaction of silicon tetrachloride with $P_7(SiMe_3)_3$ was carried out with the expected formation of compounds such as $(SiMe_3)_2P_7$-$SiCl_2$-$P_7(SiMe_3)_2$ or $P_7(SiMe_3)_2SiCl_3$ through $SiCl_3/SiMe_3$ exchange. The reaction was carried out in a vial at room temperature. Dry toluene was added to a mixture of $SiCl_4$ and $P_7(SiMe_3)_3$, and a $^{31}P$-NMR analysis was performed which showed the complete destruction of the $P_7$-backbone.

Similar results were obtained with tin tetrachloride.

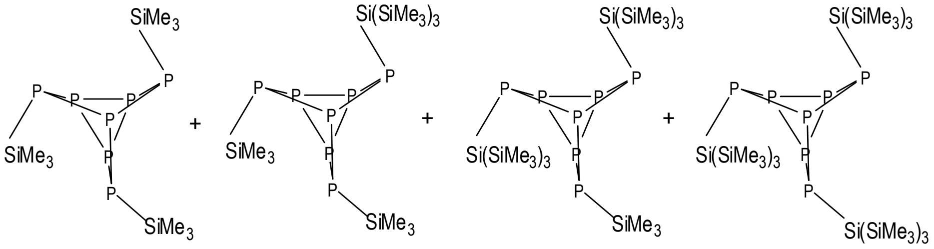
### 3.6.3 Synthesis of $(SiMe_3)_{3-n}P_7[Si(SiMe_3)_3]_n$ with n = 1,2,3



**Scheme 48: Cleavage of one Si-P bond of $P_7(SiMe_3)_3$ using $[Si(SiMe_3)_3]Cl$**

### 3.6.3.1 Synthesis of $[Si(SiMe_3)_3]P_7(SiMe_3)_2$

The reaction of $P_7(SiMe_3)_3$ with $ClSi(SiMe_3)_3$ left the $P_7$ skeleton unchanged. When the reactants were brought together in DME at -50°C in a molar ratio of 1:1, a mixture was formed consisting of $(Me_3Si)_2P_7[Si(SiMe_3)_3]$, $(Me_3Si)P_7[Si(SiMe_3)_3]_2$ and $P_7[Si(SiMe_3)_3]_3$, along with unchanged $P_7(SiMe_3)_3$ and $Me_3SiCl$. Separation by fractional crystallisation was not possible.



**Scheme 49: Structure of the four heptaphosphanes $(Me_3Si)_2P_7[Si(SiMe_3)_3]$, $(Me_3Si)P_7[Si(SiMe_3)_3]_2$, $P_7[Si(SiMe_3)_3]_3$ and $P_7(SiMe_3)_3$ present in solution.**

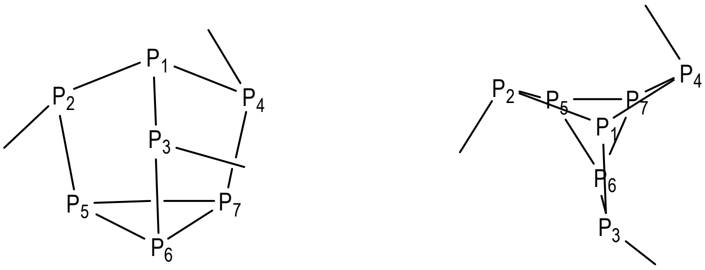


**Figure 18: Structure of $P_7(SiR_3)_3$ with $P_{5,6,7}$ = basal P-atoms, $P_{2,3,4}$ = equatorial P-atoms and $P_1$ = apical P-atom.**

The $^{31}$P-NMR spectrum of this solution shows ranges of $^{31}$P chemical shifts for the numbered phosphorus atoms (Figure 18):

(a) -145 to -170 ppm, signals of the basal P-atoms ($P_{5,6,7}$);

(b) -95 to -105 ppm, signals of the apical P-atom ($P_1$);

(c) +10 to -25 ppm, signals of the P-atoms connected to the $SiMe_3$, and $(SiMe_3)_3Si$ groups ($P_{2,3,4}$).

In heteroleptically substituted $P_7$ systems all the P-atoms are magnetically non-equivalent. In these cases, three signals are expected for the basal P-atoms ($P_b$) as well as for the equatorial P-atoms ($P_e$). In the mixture the differences between the chemical shifts of the $P_b$ and $P_e$ atoms are rather small, and so there is superposition of signals.

For $P_a$ (in all compounds) an approximate quartet of quartets is expected. As shown in Figure 19, at least two of these are superposed in signals between -90 and -110 ppm. The signals of $[Si(SiMe_3)_3]P_7(SiMe_3)_2$ and $[Si(SiMe_3)_3]_2P_7(SiMe_3)$ are observed at -102 and -104 ppm. The quartet of $P_7[Si(SiMe_3)_3]_3$ could be observed at -107 ppm and the quartet of $P_7(SiMe_3)_3$ at -99 ppm. In this reaction, the two main products were $[Si(SiMe_3)_3]P_7(SiMe_3)_2$ and $[Si(SiMe_3)_3]_2P_7(SiMe_3)$, with traces of $P_7[Si(SiMe_3)_3]_3$ and $P_7(SiMe_3)_3$. No other resonances were detected. Despite several attempts we were not able to prepare pure $[Si(SiMe_3)_3]P_7(SiMe_3)_2$ by silyl exchange.

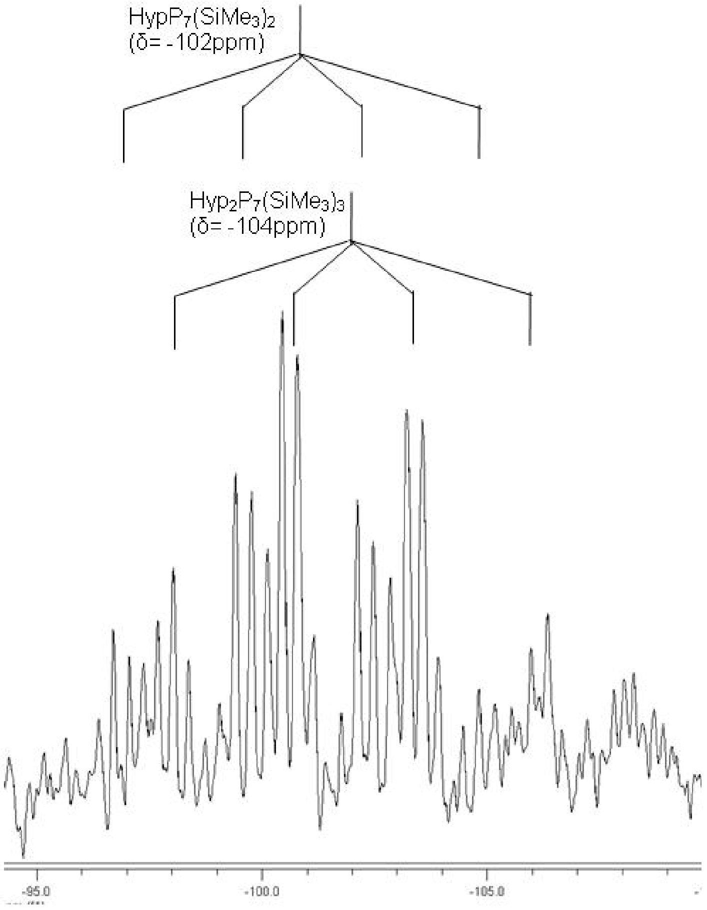
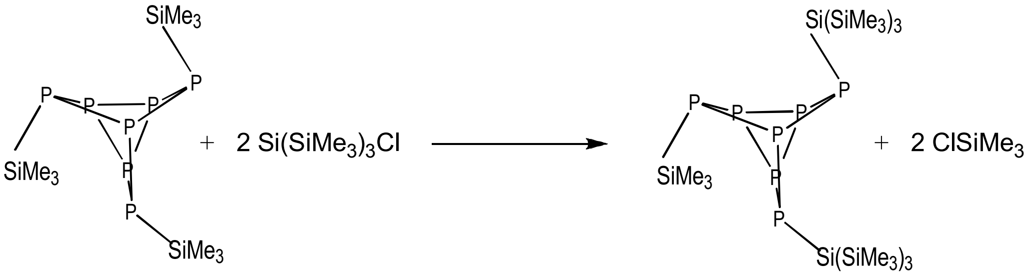


**Figure 19: Overlapping signals of the apical P-atoms in the $^{31}$P-NMR spectrum of the mixture $Hyp_nP_7(SiMe_3)_{3-n}$. (Hyp= $Si(SiMe_3)_3$).**

### 3.6.3.2 Synthesis of $[Si(SiMe_3)_3]_2P_7(SiMe_3)$



**Scheme 50: Cleavage of two Si-P bonds of $P_7(SiMe_3)_3$ using $[Si(SiMe_3)_3]Cl$.**

The reaction of $P_7(SiMe_3)_3$ and $[Si(SiMe_3)_3]Cl$ in DME at -40°C in a molar ratio 1:2 gave pure $(Me_3Si)P_7[Si(SiMe_3)_3]_2$. The same result was obtained when the reaction was carried out in toluene or THF. Contrary to the observations of H.G von Schnering, the result of the reaction was independent of the solvent. [100] Obviously, the driving force of the reaction is the stabilisation of the $P_7$-cage by the hypersilyl substituent.

Only traces of $P_7[Si(SiMe_3)_3]_3$ were detected which certainly was due to the sufficient steric protection of the $SiMe_3$-substituent by the two hypersilyl groups $Si(SiMe_3)_3$. Also due to the steric effect only the symmetric isomer was observed. The substitution of $(Me_3Si)$-substituent by the $Si(SiMe_3)_3$-substituent occured without change of the symmetry of the $P_7$-backbone. The $^{31}P$-NMR spectrum of the compound is shown in Figure 20 and displays four groups of signals:

(a) -145 ppm, signal of a basal P-atom ($P_b$),

(b) -170 ppm, signal of two others P-atoms ($P_b$),

(c) -105 ppm, signal of the apical P-atom ($P_a$); a pure quartet confirms the presence of only one product.

(d) +10 to -25 ppm, three signals for the P-atoms connected to the $-SiMe_3$ and $–Si(SiMe_3)_3$ groups ($P_e$).

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[100] Mujica, C.; Weber, D.; v. Schnering, H. G.; *Z. Naturforsch.* **1986**, 41B, 991.

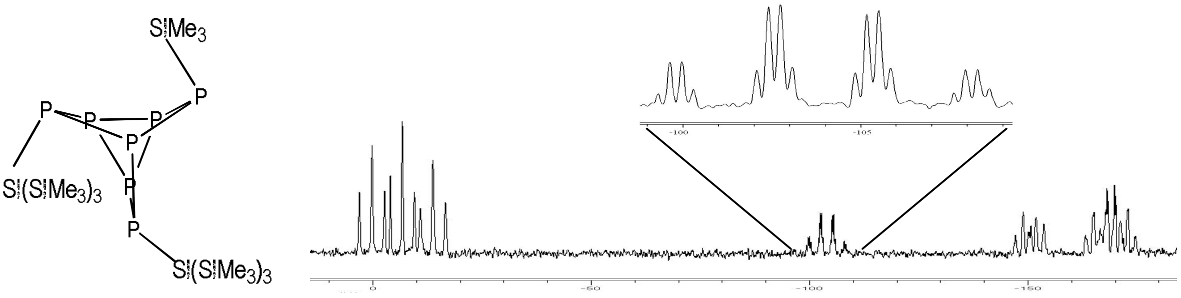
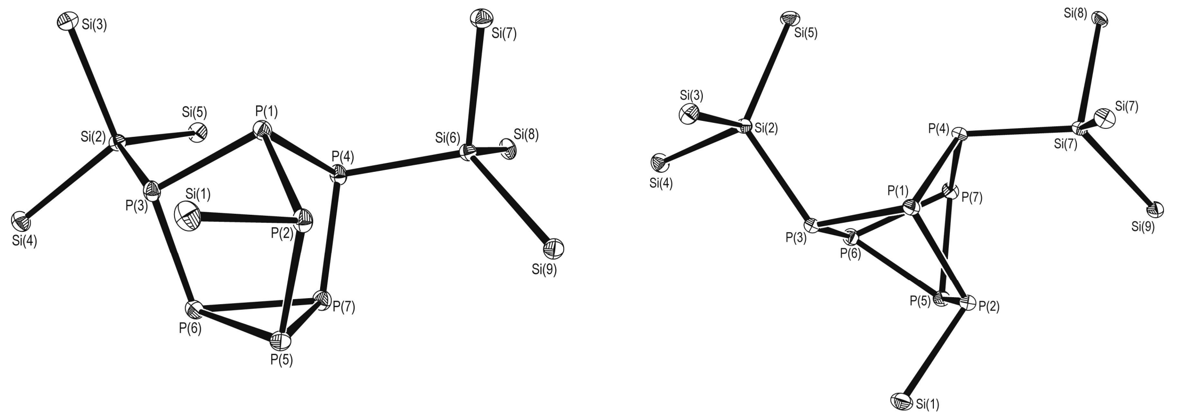


Figure 20: Structure and $^{31}$P-NMR spectrum of pure $[Si(SiMe_3)_3]_2P_7(SiMe_3)$ in toluene.

### 3.6.3.3 Crystal structure of $[Si(SiMe_3)_3]_2P_7(SiMe_3)$

Crystallization from toluene afforded crystals with a quality sufficient for the determination of the molecular structure by X-ray diffraction. The compound is chiral and crystallizes as a racemic modification. An ORTEP plot of the molecular structure as well as the arrangement of the racemic pair in the crystal is presented in Figure 21, including selected bond lengths and bond angles. It is the first structure of a heteroleptic neutral cage $P_7R_2R'$ (R unlike R'). Despite the considerable difference in the steric demand of a $SiMe_3$ and a $Si(SiMe_3)_3$ group, no distortion of the $P_7$-cage from local $C_{3v}$ symmetry is observed. Only the PPSi angles P1P2Si1, P1P3Si2 and P1P4Si7 differ markedly from each other (see caption of Figure 21).



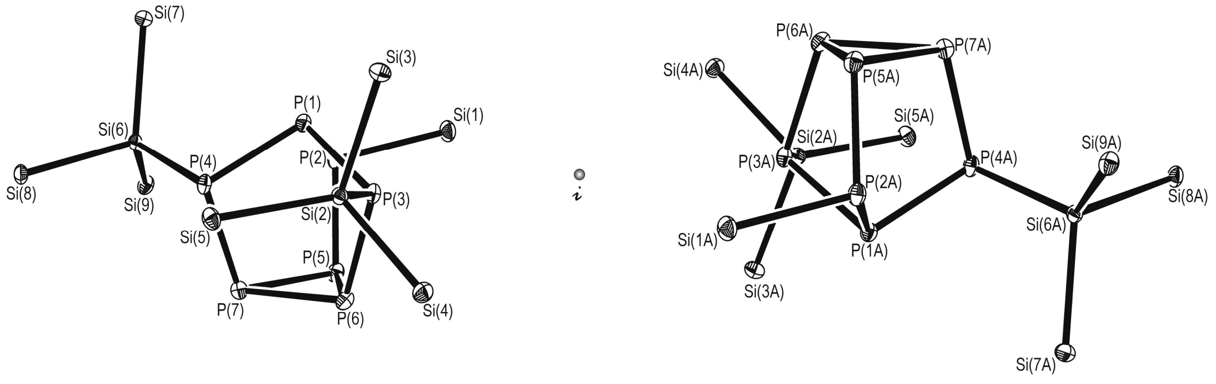
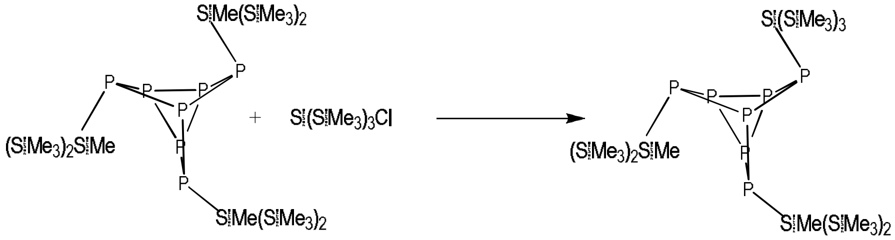


**Figure 21: ORTEP plot (30% probabilities, side view and top view) of the molecular structure of $[(SiMe_3)_3Si]_2P_7SiMe_3$ and arrangement in the crystal. $CH_3$-groups have been omitted for clarity. Important bond lenghts (pm) and bond angles (°) are: P1-P2: 217.63(6); P1-P3: 217.84(6); P1-P4: 217.34(6); P2-P5: 219.99(7); P3-P6: 219.48(7); P4-P7: 220.07(7); P5-P6: 221.67(7); P6-P7: 220.03(7); P5-P7: 221.58(7); P2-Si1: 228.42(7); P3-Si2: 227.84(6); P4-Si6: 229.57(6); P2-P1-P4: 97.15(3); P2-P1-P3: 97.90(2); P3-P1-P4: 99.30(3); P1-P2-P5: 102.62(3); P1-P3-P6: 102.56(3); P1-P4-P7: 102.57(2); P5-P6-P3: 100.32(3); P2-P5-P7: 100.15(2); P4-P7-P6: 100.97(3); P7-P6-P3: 107.28(3); P2-P5-P6: 107.00(3); P4-P7-P5: 106.72(3); P1-P2-Si1: 104.31(3); P1-P3-Si2: 110.95(2); P1-P4-Si6: 107.22(3).**

### 3.6.4 Synthesis of $[SiMe(SiMe_3)_2]_{3-n}P_7[Si(SiMe_3)_3]_n$ with n = 1,2,3

#### 3.6.4.1 Synthesis of $[SiMe(SiMe_3)_2]_2P_7[Si(SiMe_3)_3]$



**Scheme 51: Cleavage of one Si-P bond of $P_7(SiMe(SiMe_3)_2)_3$ using $Si(SiMe_3)_3Cl$.**

As expected the reaction of $P_7(SiMe(SiMe_3)_2)_3$ with $ClSi(SiMe_3)_3$ left the $P_7$ skeleton unchanged. When the reactants were brought together in DME at -50°C in a molar ratio 1:1, a mixture of heptaphosphanes was formed consisting of $[SiMe(SiMe_3)_2]_2P_7[Si(SiMe_3)_3]$, $[SiMe(SiMe_3)_2]P_7[Si(SiMe_3)_3]_2$, along with unchanged $[SiMe(SiMe_3)_2]_3P_7$ and $Si(SiMe_3)_3Cl$. The presence of $P_7[Si(SiMe_3)_3]_3$ in solution could not be observed. Here again, separation of the different derivatives by fractional crystallisation was not successful. As the mixture of products did not dissolve sufficiently in DME, the NMR analysis was carried out in toluene. The $^{31}$P-NMR spectrum of this solution shows three sets of signals:

(a) -160 to -170 ppm, signals of the basal P-atoms ($P_{5,6,7}$);

(b) -85 to -110 ppm, signals of the apical P-atom ($P_1$);

(c) +10 to -25 ppm, signals of the equatorial P-atoms connected to the $Si(SiMe_3)_3$ and $(SiMe_3)_2SiMe$ groups ($P_{2,3,4}$).

In $[SiMe(SiMe_3)_2]_nP_7[Si(SiMe_3)_3]_{3-n}$ (n = 1, 2, 3) all the P-atoms are magnetically non-equivalent but superposition of signals for $P_b$ as well as for $P_e$ is observed. For $P_a$ (in all compounds) at least three quartets are superimposed in the shift range between -80 and -105 ppm. The two main products were $Si(SiMe_3)_3P_7[SiMe(SiMe_3)_2]_2$ and $[Si(SiMe_3)_3]_2P_7SiMe(SiMe_3)_2$, with small quantities of $P_7[Si(SiMe_3)_3]_3$. No other resonances were observed (Figure 22).

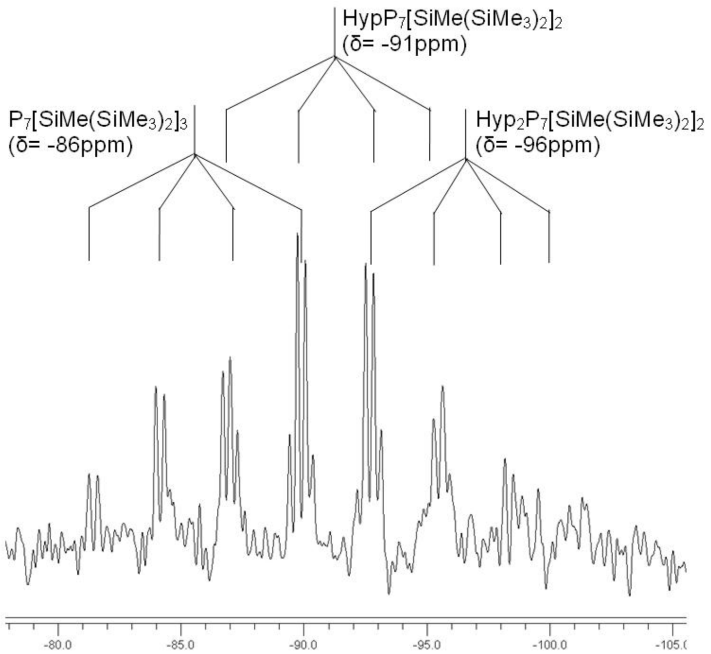


**Figure 22: Overlapping signals of the apical P-atoms in the $^{31}$P-NMR spectrum of the mixture $Hyp_nP_7[SiMe(SiMe_3)_2]_{3-n}$. (Hyp= $Si(SiMe_3)_3$).**

### 3.6.4.2 Synthesis of $SiMe(SiMe_3)_2P_7[Si(SiMe_3)_3]_2$

**Scheme 52: Cleavage of two Si-P bonds of $P_7[SiMe(SiMe_3)_2]_3$ using two equivalents of $ClSi(SiMe_3)_3$.**

The reaction of $P_7[SiMe(SiMe_3)_2]_3$ with $ClSi(SiMe_3)_3$ in DME at -40°C in a molar ratio 1:2 led to pure $SiMe(SiMe_3)_2P_7[Si(SiMe_3)_3]_2$. The compound $P_7[Si(SiMe_3)_3]_3$ was not detected in the $^{31}$P-NMR spectrum obviously due to the steric protection of the third Si-P bond by the bulky $Si(SiMe_3)_3$-substituents. According to the NMR analysis, only the symmetric isomer was observed. The substitution of the $SiMe(SiMe_3)_2$-substituent by the $Si(SiMe_3)_3$-substituent occurred without change of $P_7$-backbone. The formation of only one isomer can be explained by the steric interaction of the large oligosilyl groups.

The $^{31}$P-NMR spectrum shows four second-order signals of relative intensity 1:2:1:3 (Figure 23):

(a) 4.1 ppm, signal of an equatorial P-atom ($P_e$),

(b) -8.3 ppm, signal of two equatorial P-atoms ($P_e$),

(c) -96 ppm, pure quartet of the apical P-atom ($P_a$),

(d) -165 ppm, signals of the three basal P-atoms ($P_b$).

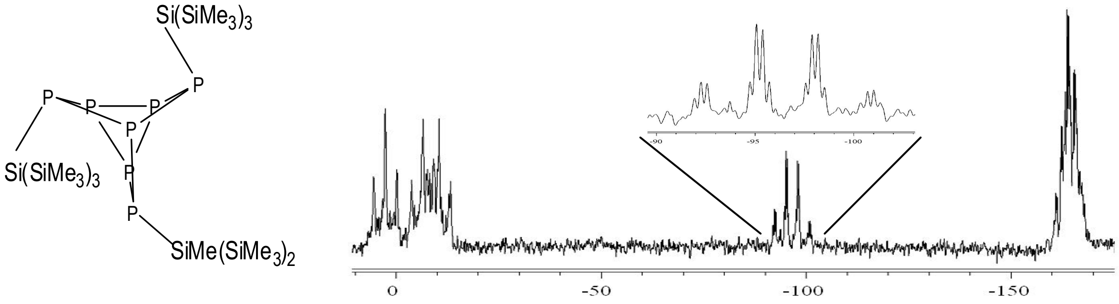


**Figure 23: $^{31}$P-NMR spectrum of pure $[Si(SiMe_3)_3]_2P_7SiMe(SiMe_3)_2$ in toluene.**

### 3.6.4.3 Crystal structure of $SiMe(SiMe_3)_2P_7[Si(SiMe_3)_3]_2$

Crystallization from toluene afforded crystals with a quality sufficient for the determination of the molecular structure by X-ray diffraction. The compound is chiral and crystallizes as a racemic modification. An ORTEP plot of the molecular structure is presented in Figure 24, including selected bond lengths and bond angles. No distortion of the $P_7$-cage from local $C_{3v}$ symmetry is observed. As observed for $SiMe_3P_7[Si(SiMe_3)_3]_2$, only the PPSi angles P1P2Si1, P1P3Si4 and P1P4Si8 differ markedly from each other (see caption of Figure 24).

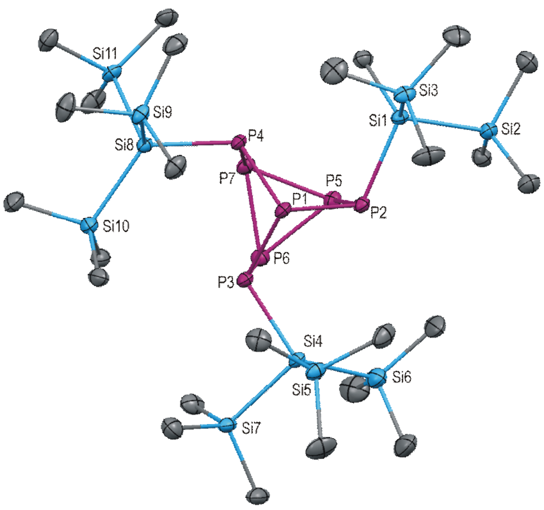
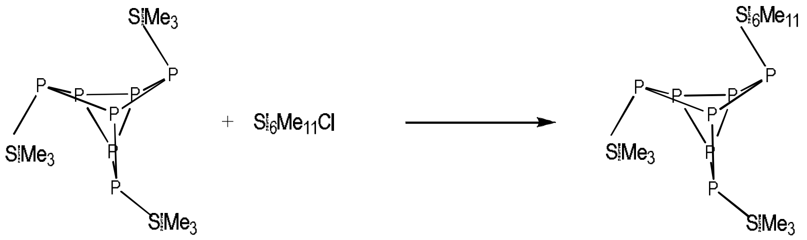


**Figure 24: ORTEP plot (30% probabilities, top view) of the molecular structure of $SiMe(SiMe_3)_2P_7[Si(SiMe_3)_3]_2$ and arrangement in the crystal. Important bond lenghts (pm) and bond angles (°) are: P1-P4: 2.1826(18); P1-P2: 2.1842(18); P1-P3: 2.1878(19); P4-P7: 2.201(2); P5-P2: 2.1991(19); P5-P6: 2.2110(19); P5-P7: 2.2222(19); P3-P6: 2.1913(19); P7-P6: 2.2180(19); P2-Si1: 2.2879(19); P3-Si4: 2.2883(19); P4-Si8: 2.2864(18); P2-Si1: 2.2879(19); P3-Si4: 2.2883(19); P4-Si8: 2.2864(18); P2-P1-P4: 97.15(3); P2-P1-P3: 97.90(2); P3-P1-P4: 99.30(3); P1-P2-P5: 102.62(3); P1-P3-P6: 102.56(3); P1-P4-P7: 102.57(2); P5-P6-P3: 100.32(3); P2-P5-P7: 100.15(2); P4-P7-P6: 100.97(3); P7-P6-P3: 107.28(3); P2-P5-P6: 107.00(3); P4-P7-P5: 106.72(3); P1-P2-Si1: 104.31(3); P1-P3-Si4: 110.95(2); P1-P4-Si8: 107.22(3).**

### 3.6.5 Synthesis of $P_7(SiMe_3)_{3-n}(Si_6Me_{11})_n$ with n = 1,2,3

#### 3.6.5.1 Synthesis of $(Si_6Me_{11})P_7(SiMe_3)_2$



**Scheme 53: Cleavage of one Si-P bond of $P_7(SiMe_3)_3$ using one equivalent $ClSi_6Me_{11}$.**

The cleavage of one or more Si-P bonds by $ClSi(SiMe_3)_3$ left the $P_7$ skeleton unchanged as observed above with the reaction of $P_7[SiMe(SiMe_3)_2]_3$ and $P_7(SiMe_3)_3$.

In order to synthesize other heteroleptically substituted heptaphosphanes, the bulky group $ClSi_6Me_{11}$ was used in place of the hypersilyl group for silyl exchange.

The reaction of $P_7(SiMe_3)_3$ with $SiMe_{11}Cl$ at -50°C in a molar ratio 1:1 led to a mixture of heptaphosphanes. The reaction was slow and the mixture was stirred at room temperature for 4 days. A $^{31}$P-NMR was performed and a mixture of the compounds $P_7(SiMe_3)_2(Si_6Me_{11})$, $(SiMe_3)P_7(Si_6Me_{11})_2$, $P_7(Si_6Me_{11})_3$ and $P_7(SiMe_3)_3$ was observed.

The $^{31}$P-NMR spectrum of this solution shows signals in three ppm ranges:

(a) -145 to -180 ppm, signals of the basal P-atoms ($P_{5,6,7}$);

(b) -80 to -105 ppm, signals of the apical P-atom ($P_1$); four overlapping quartets are discerned for $P_1$ which confirm a mixture in solution of $P_7(SiMe_3)_2(Si_6Me_{11})$, $(SiMe_3)P_7(Si_6Me_{11})_2$, $P_7(Si_6Me_{11})_3$ and $P_7(SiMe_3)_3$ (Figure 25).

(c) +5 to -10 ppm, signals of the P-atoms connected to the $-SiMe_3$ and $-Si_6Me_{11}$groups ($P_{2,3,4}$).

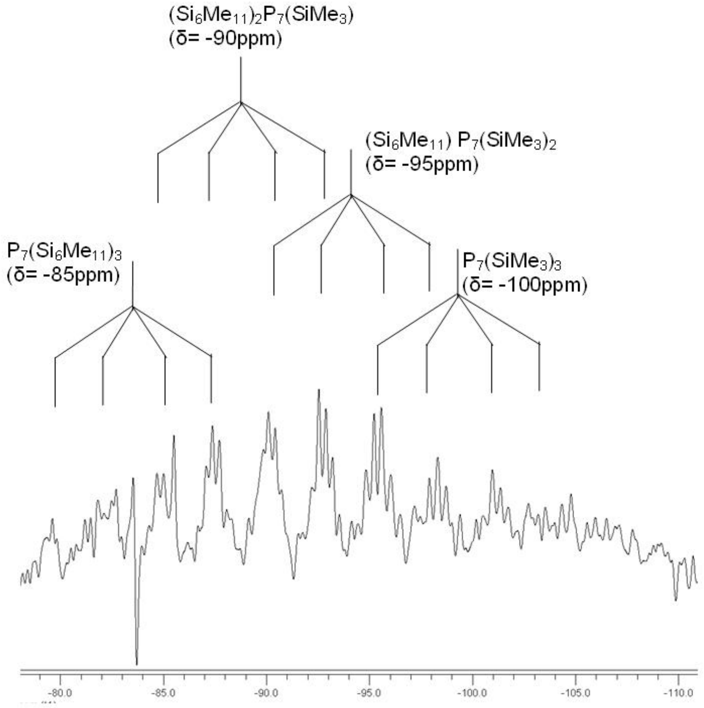


**Figure 25: Overlapping signals of the apical P-atoms in the $^{31}$P-NMR spectrum of the mixture $(Si_6Me_{11})_nP_7(SiMe_3)_{3-n}$.**

### 3.6.5.2 Synthesis of $P_7(Si_6Me_{11})_3$

**Scheme 54: Cleavage of one Si-P bond of $P_7(SiMe_3)_3$ using three equivalents of $ClSi_6Me_{11}$.**

When $P_7(SiMe_3)_3$ and $Si_6Me_{11}Cl$ were brought together in DME at -50°C in a molar ration 1:3, $P_7(Si_6Me_{11})_3$ was formed:

The $^{31}P$ NMR spectrum shows three signals:

(a) -169 ppm, signal of the basal P-atoms ($P_{5,6,7}$);

(b) -84 ppm, signal of the apical P-atom ($P_1$);

(c) 0 ppm, signal of the P-atoms connected to the $Si_6Me_{11}$ groups ($P_{2,3,4}$).

A pure quartet is observed for $P_1$ which confirm the presence of just one product.

The analysis of the $^{29}Si$ NMR spectrum shows no trace of a $SiMe_3$ bearing compound.

According to the result of G.Tekautz [37], the $^{31}P$-NMR spectrum displays the typical signals for pure $P_7(Si_6Me_{11})_3$. No other resonances were detected ruling out the presence of larger quantities of $P_7(SiMe_3)_2(Si_6Me_{11})$, $(SiMe_3)P_7(Si_6Me_{11})_2$ and $P_7(SiMe_3)_3$.

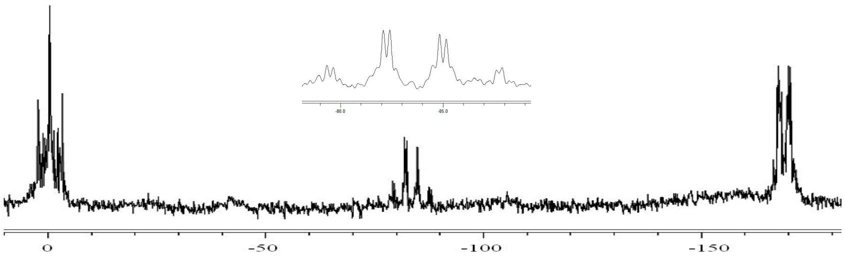


**Figure 26: $^{31}P$-NMR spectrum from $P_7(Si_6Me_{11})_3$ in toluene.**

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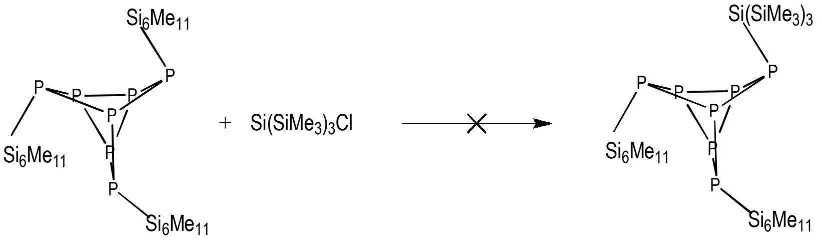
[37] Tekautz, G; *Thesis, T.U Graz*, **2005**

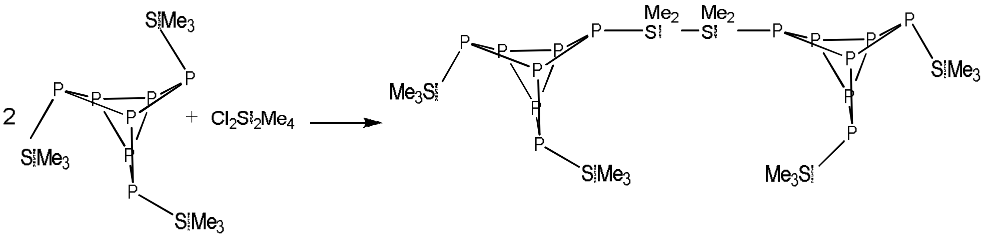
### 3.6.6 Synthesis of $(Si_6Me_{11})_2P_7Si(SiMe_3)_3$



**Scheme 55: Cleavage of one Si-P bond of $P_7(Si_6Me_{11})_3$ using one equivalent $ClSi(SiMe_3)_3$.**

No reaction was observed when $P_7(Si_6Me_{11})_3$ and $ClSi(SiMe_3)_3$ were brought together in toluene or in DME in a molar ratio 1:1. This was also the case when an excess of $ClSi(SiMe_3)_3$ was used or the mixture was heated to reflux for a couple of days. Quite obviously, the $Si_6Me_{11}$ group is bulky enough to protect efficiently the P-Si bond from the attack of $ClSi(SiMe_3)_3$.

### 3.6.7 Synthesis of $(SiMe_3)_2P_7(Si_2Me_4)P_7(SiMe_3)_2$



**Scheme 56: Synthesis of $(SiMe_3)_2P_7(Si_2Me_4)P_7(SiMe_3)_2$ by silyl exchange between $P_7(SiMe_3)_3$ and $Cl_2Si_2Me_4$.**

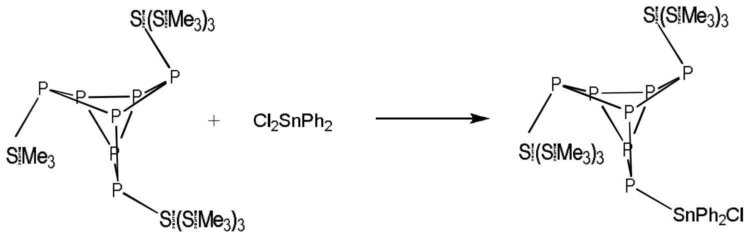
$(SiMe_3)_2P_7(Si_2Me_4)P_7(SiMe_3)_2$ could also be prepared by a silyl exchange reaction between $P_7SiMe_3$ and $Cl_2Si_2Me_4$ when the reactants were used in a molar ratio 2:1. Besides chlorotrimethylsilane, the only product was $(SiMe_3)_2P_7(Si_2Me_4)P_7(SiMe_3)_2$, according to the $^{31}$P-NMR spectrum shown in Figure 29 (page 84) which is identical with the one presented in Figure 16.

Quite interestingly, with a large excess of $Cl_2Si_2Me_4$ an insoluble polymeric material formed, consisting of a network of $P_7$-cages connected by $SiMe_2$-$SiMe_2$ spacers. An infrared spectrum of the solid clearly showed that the absorptions in the range 500 – 280 cm$^{-1}$, which are characteristic for the $P_7$ structural unit are still present.

Moreover, an inspection of the region of the SiC stretching bands ($v_sSiC_3$: 630 cm$^{-1}$; $v_sSiC_2$: 660 cm$^{-1}$) reveals that the polymer contains no $SiMe_3$-groups

## 3.7 Derivatization of $(SiMe_3)P_7[Si(SiMe_3)_3]_2$

### 3.7.1 Reaction of $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ with $Cl_2SnPh_2$



**Scheme 57: Proposed reaction between $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ and $Cl_2SnPh_2$.**

The reaction of $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ with $Cl_2SnPh_2$ in a molar ratio 2:1 was expected to give $[Si(SiMe_3)_3]_2P_7SnPh_2P_7[Si(SiMe_3)_3]_2$, which consist of two $P_7[Si(SiMe_3)_3]_2$ cages connected by a diphenyltin bridge. The reactants were brought together, and dry toluene was added dropwise to the mixture at low temperature. After stirring for two days, the $^{31}$P-NMR spectrum shown in Figure 27 was obtained. The typical signal of the starting material $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ could be observed as well as two others signals at 20 ppm and 10 ppm. A mixture of two compounds was formed. The solution was stirred for one month but no advancement in the reaction occurred. The presence of unreacted $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ indicated that obviously due to the bulkiness of this $P_7$-cage, $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ could only react with $Cl_2SnPh_2$ in a ratio 1:1 forming $[Si(SiMe_3)_3]_2P_7(SnPh_2)Cl$. This compound could not further react with an other $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ to form $[Si(SiMe_3)_3]_2P_7SnPh_2P_7[Si(SiMe_3)_3]_2$ due to the size of the two reactants.

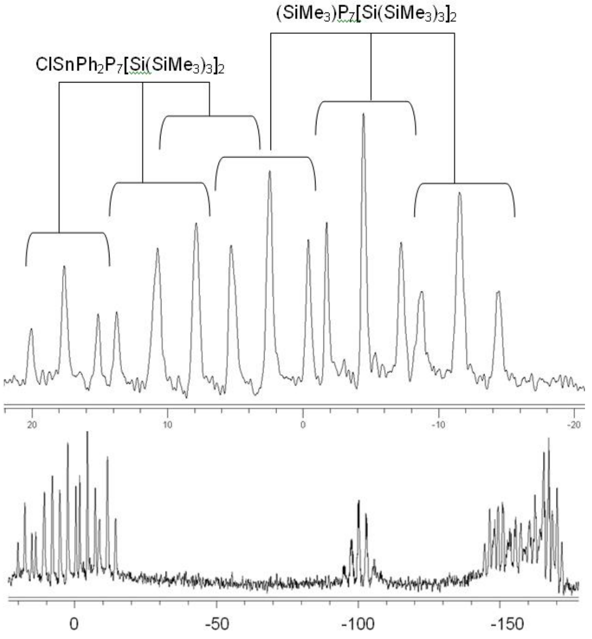


**Figure 27: $^{31}$P-NMR spectrum (top) and expansion of the range 20ppm to -20ppm (bottom) of a mixture of $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ and $[Si(SiMe_3)_3]_2P_7(SnPh_2)Cl$.**

This observation was confirmed when the reaction was performed in a molar ratio 1:1. In this case, the $^{31}$P-NMR spectrum shown in Figure 28 was obtained.

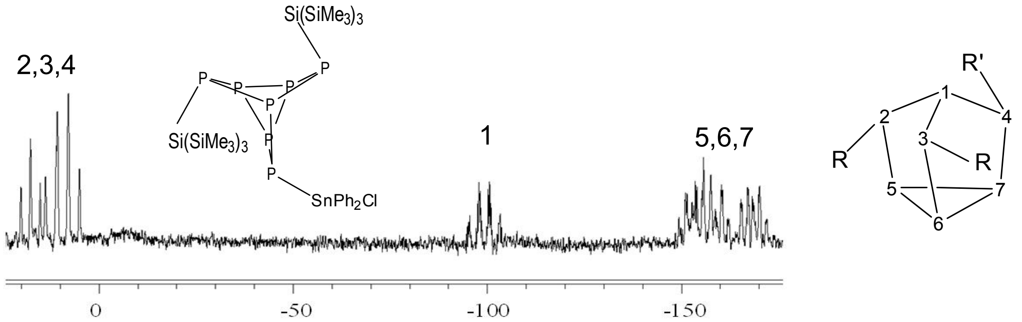


**Figure 28: $^{31}$P-NMR spectrum of $[Si(SiMe_3)_3]_2P_7(SnPh_2)Cl$. R= $Si(SiMe_3)_3$.and R'=$SnPh_2Cl$**

The $^{31}$P-NMR spectrum displays five sets of signals of relative intensities 1:2:1:2.1. The equatorial P-atoms bearing the -$Si(SiMe_3)_3$ and -$SnPh_2Cl$ groups give resonances between +20 and +5 ppm. The resonance of the P-atom bonded to Sn is in accordance with the literature. [100] The apical P-atom gives a pure quartet at -100 ppm; the pure quartet confirms the presence of only one product in solution. The three basal P-atoms give signals at -155 and -170 ppm. The $^{31}$P-NMR spectrum and $^{29}$Si-NMR spectrum are consistent with the proposed structure schemed above.

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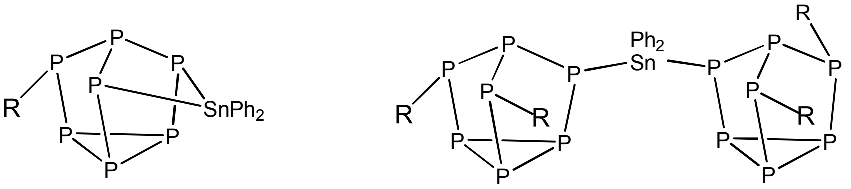
[100] Mujica, C.; Weber, D; v. Schnering, H. G; *Z. Naturforsch.* **1986**, 41B, 991.

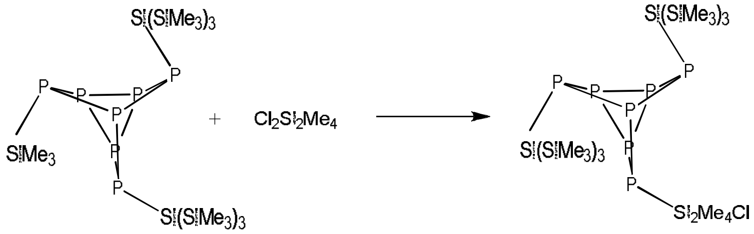
According to the spectrum, the $P_7$ skeleton is symmetrically substituted. Crystals could not be obtained.

The target compound $[Si(SiMe_3]_2P_7SnPh_2P_7[Si(SiMe_3]_2$ which consists of two $P_7$ cages connected by a tin bridge was not obtained by using the molar ratio 2:1. A mixture of $[Si(SiMe_3)_3]_2P_7(SnPh_2)Cl$ and $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ was obtained. Using a large excess of diphenyltinchloride, the reaction duration could be decreased in a significant way, from a couple of days to a couple of hours. No further advancement in the reaction was observed, nor rearrangement or secondary reactions. The P-atoms bonded to the $Si(SiMe_3)_3$ groups are effectively shielded and do not react with the excess of $SnPh_2Cl$. None of the possible heptaphosphanes $[Si(SiMe_3)_3]P_7[(SnPh_2)Cl]_2$ or $P_7[(SnPh_2)Cl]_3$ were detected. The formation of $[Si(SiMe_3)_3]P_7(SnPh_2)$ was also not observed.



**Scheme 58: Structure of $[Si(SiMe_3)_3]P_7(SnPh_2)$ and $[Si(SiMe_3]_2P_7SnPh_2P_7[Si(SiMe_3]_2$ which were not formed.**

### 3.7.2 Reaction of $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ with $Cl_2Si_2Me_4$



**Scheme 59: Formation of $[Si(SiMe_3)_3]_2P_7(Si_2Me_4)Cl$ by silyl exchange reaction.**

Based on the results obtained from reaction of $Cl_2Si_2Me_4$ with $P_7(SiMe_3)_3$ leading to $(SiMe_3)_2P_7(Si_2Me_4)P_7(SiMe_3)_2$, the reaction of $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ with $Cl_2Si_2Me_4$ was expected to give $[Si(SiMe_3)]_2P_7(Si_2Me_4)P_7[Si(SiMe_3)]_2$. $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ was added to a toluene solution of $Cl_2Si_2Me_4$ at very low temperature in a molar ratio 2:1. A reaction occurred but didn't lead to the target product. As observed for the reaction of $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ with $Cl_2SnPh_2$, the typical signals of the starting material $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ were still present even if the reaction was stirred for two weeks.

When the reactants were brought together in a molar ratio 1:1, the $^{31}$P-NMR spectrum of the solution (Figure 29, **C**) displayed the typical signals of silylated heptaphosphanes $P_7(SiR_3)_3$. According to the $^{31}$P-NMR spectrum, $[Si(SiMe_3)_3]_2P_7(Si_2Me_4)Cl$ was obviously formed. A proposed pathway was that one cage reacted first to form the compound $[Si(SiMe_3)_3]_2P_7(Si_2Me_4)Cl$ in which the Si-Cl bond could not react further with an other $P_7$-cage due to the unfavourable steric interaction between $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ and $[Si(SiMe_3)_3]_2P_7(Si_2Me_4)Cl$. This pathway explains the presence of the starting material when the reaction was performed in a molar ratio 2:1.

The $^{31}$P-NMR spectrum obtained is shown in Figure 29 **(C)**. Five signals of relative intensity 1:2:1:1:2 are observed. The three equatorial P-atoms bearing the hypersilyl-group and the $(Si_2Me_4)Cl$ groups give resonances at -10 and +5 ppm. Three other signals are present: two signals for the basal P-atoms at -155 pm (1P) and -170 ppm (2P), and the typical quartet of the apical P-atom at -100 ppm. The pure quartet indicates that just one product was present in solution. Figure 29 shows the typical spectra of $(SiMe_3)_2P_7(Si_2Me_4)P_7(SiMe_3)_2$ **(A)** and $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ **(B).** Spectrum (**C)**, which is similar to **(B)**, displays typical signals of a $P_7R_2R'$ heptaphosphane ( R unlike R'),

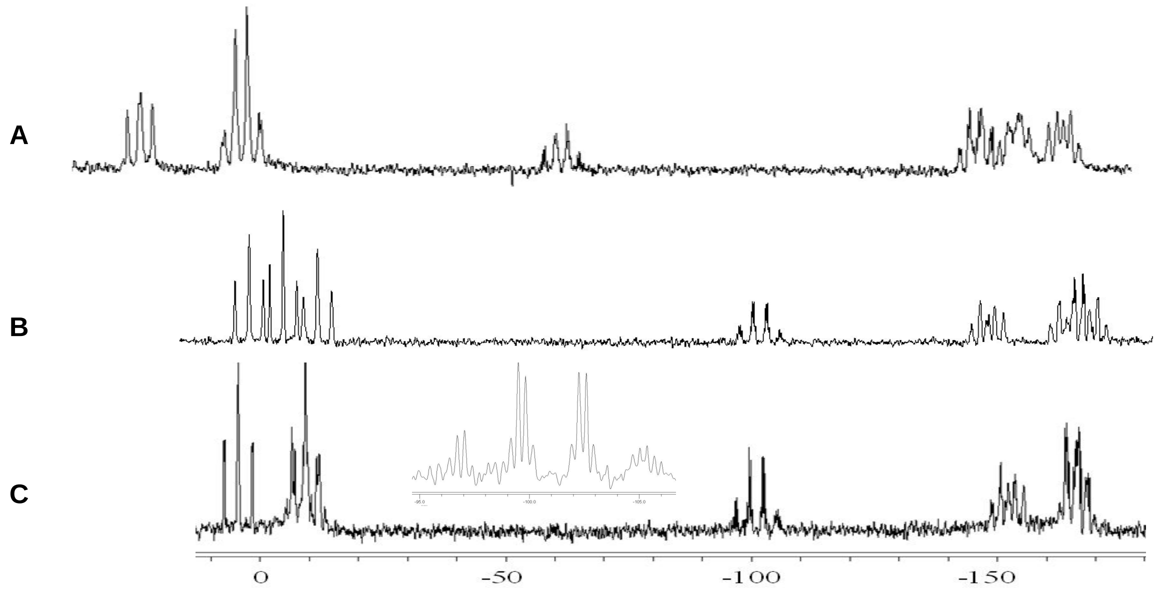
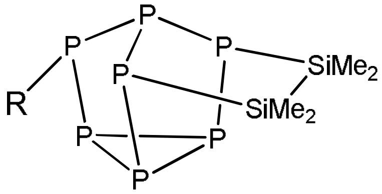


**Figure 29: $^{31}$P-NMR spectrum of $(SiMe_3)_2P_7(Si_2Me_4)P_7(SiMe_3)_2$ (A), $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ (B) and $[Si(SiMe_3)_3]_2P_7(Si_2Me_4)Cl$ (C).**

With a large excess of $Cl_2Si_2Me_4$ added at room temperature, no further reaction or rearrangement of the $P_7$-backbone could be observed. The Si-P bond quite obviously is well protected by the bulky $Si(SiMe_3)_3$ groups.

Noteworthy no reaction occurred when $P_7[Si(SiMe_3)_3]_3$ and $(Si_2Me_4)Cl_2$ were brought together. This result reinforced the presence in solution of $[Si(SiMe_3)_3]_2P_7(Si_2Me_4)Cl$ and explains why the compound $[Si(SiMe_3)_3]P_7(Si_2Me_4)$ schemed below is not formed:



**Scheme 60: Possible structure of $[Si(SiMe_3)_3]P_7(Si_2Me_4)$.**

This observation was also reinforced by the results of Fritz who synthesized $P(SiMe_3)_2$-$SiMe_2Cl$ by mixing $LiP(SiMe_3)_2$ and $Cl_2SiMe_2$ in molar ratio 1:1. [51]

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[51] Fritz, G.; Hölderich, W.; *Z. Anorg. Allg. Chem.* **1977**, 431, 76.

### 3.7.3 Synthesis of $XP_7[Si(SiMe_3)_3]_2$ with X= Cl, Br, I

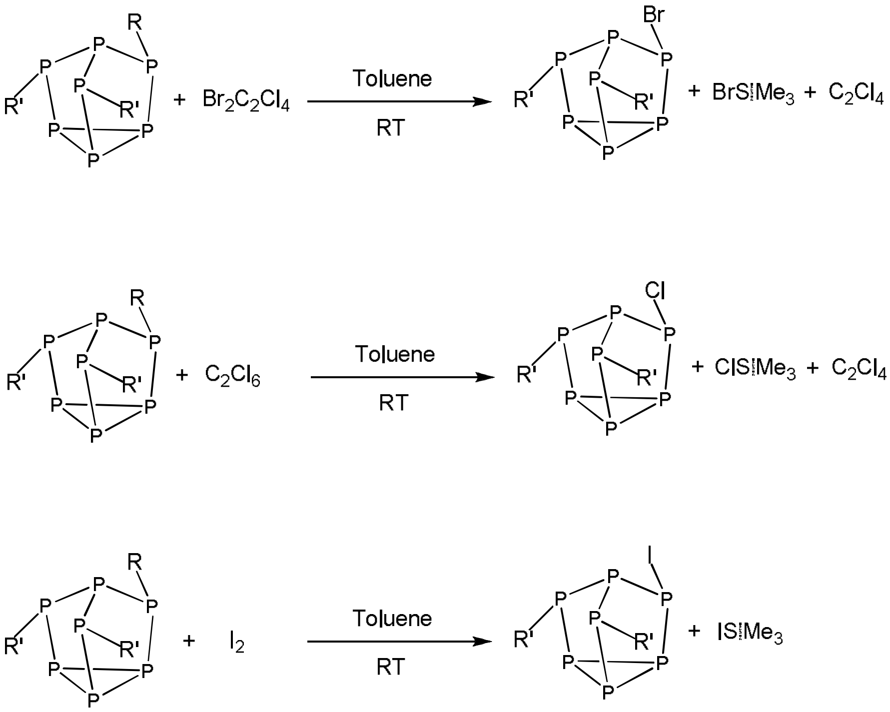
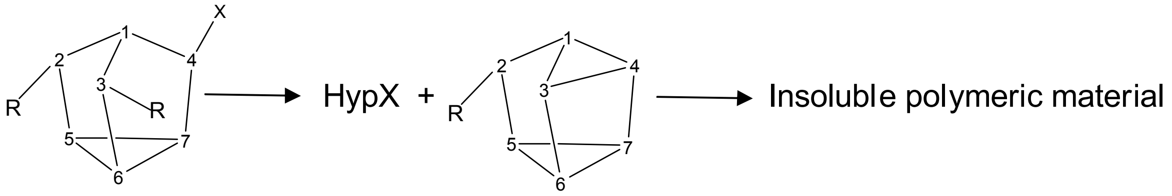


**Figure 30: Synthesis of $R_2P_7X$ (with X= Cl, Br, I). R= $SiMe_3$ R'= $Si(SiMe_3)_3$**

Halogenated cages such as $R_2P_7X$ (with X = Cl, Br, I) are valuable potential synthons for further synthesis. With organic or organometallic Li-compounds heteroleptically substituted heptaphosphanes are expected to from.

The reaction of $(SiMe_3)P_7[Si(SiMe_3)_3]_2$ with $Br_2C_2Cl_4$, $C_2Cl_6$ and $I_2$ in toluene kept the $P_7$-backbone unchanged and led to the halogenated heptaphosphanes $BrP_7[Si(SiMe_3)_3]_2$, $ClP_7[Si(SiMe_3)_3]_2$ and $IP_7[Si(SiMe_3)_3]_2$ respectively. These cages are the first heteroleptically substituted heptaphosphanes bearing a halogen atom.

The reaction occurred via the cleavage of the $SiMe_3$-P bond by $Br_2C_2Cl_4$, $C_2Cl_6$ and $I_2$. Reaction rates of the P-Si bond of the trimethylsilyl group are much faster than of the hypersilyl group. The reaction duration was about one week at 40°C for the three reagents and led to $XP_7[Si(SiMe_3)_3]_2$ according to the $^{31}$P-NMR spectrum of the solution. The $^{29}$Si-NMR spectrum showed the presence of $XSiMe_3$ as well as some $XSi(SiMe_3)_3$. The formation of an insoluble material was also observed. Obviously $XP_7Si(SiMe_3)$ slowly decomposed to an insoluble polymer under formation of HypX (Scheme 61).



**Scheme 61: Possible formation and polymerisation of $XP_7(Si(SiMe_3)_3)_2$.**

The toluene solution contained pure $XP_7[Si(SiMe_3)_3]_2$ as the only soluble phosphorus compound, according to the $^{31}$P-NMR spectrum. The formation of di-and trihalogenated cages of the type $RP_7X_2$ and $P_7X_3$ (X=Br, Cl, I) was not observed in the three cases. This is explained by the size of the hypersilyl substituent which protects the P-Si bond. The halosilanes $XSiMe_3$ produced during the reaction could be eliminated by evaporation i.v. without degradation of $XP_7[Si(SiMe_3)_3]_2$. The halogenated $P_7$-compounds gave typical $^{31}$P-NMR spectra shown in Figure 31.

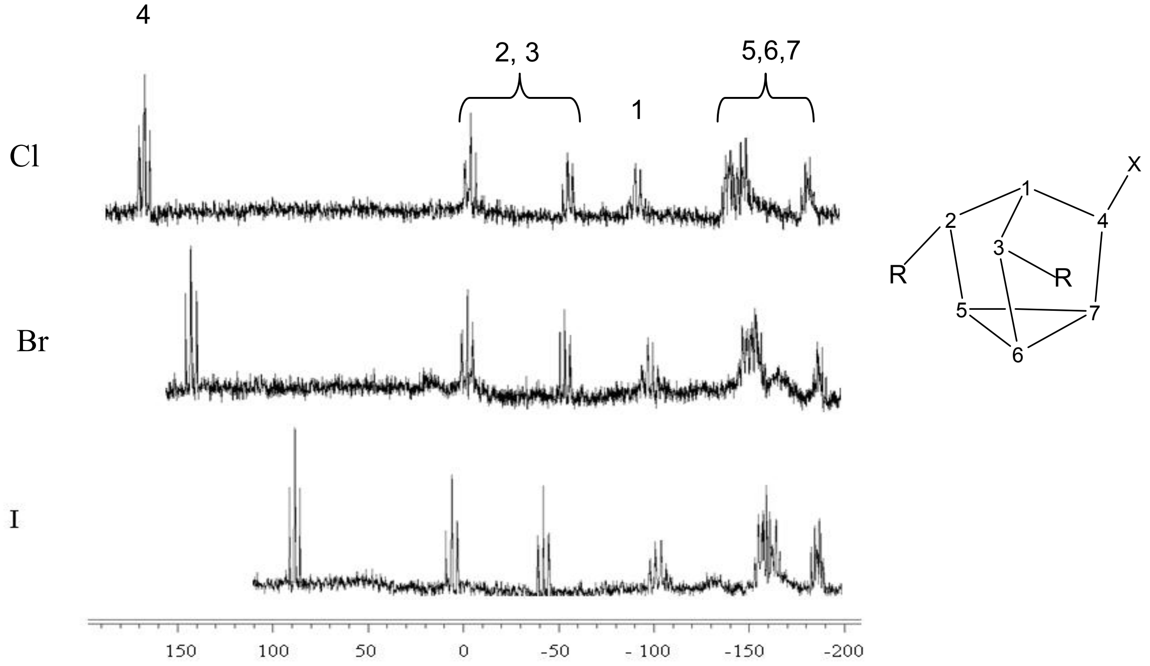


**Figure 31: $^{31}$P-NMR spectrum of $ClP_7[Si(SiMe_3)_3]_2$, $BrP_7[Si(SiMe_3)_3]_2$, $IP_7[Si(SiMe_3)_3]_2$ and numbering of the phosphorus atoms. R= $Si(SiMe_3)_3$, X= Cl, Br, I.**

The spectra of $BrP_7[Si(SiMe_3)_3]_2$ and $IP_7[Si(SiMe_3)_3]_2$ consist of six second order resonances with relative intensities 1:1:1:1:2:1. For $ClP_7[Si(SiMe_3)_3]_2$, seven signals of relative intensities 1:1:1:1:1:1:1 are observed. The equatorial P-atoms bearing the $Si(SiMe_3)_3$ substituent give signals in the range 0 ppm (2) and -45/-55 ppm (3). The equatorial P-atom carrying the halogen atom gives a signal (triplet) at +86 ppm for P-I (4). This signal shifts downfield by about 50 ppm for Br and 90 ppm for Cl. The apical

P-atom which is bonded to the three equatorial phosphorus atoms gives a quartet at -97 ppm (1). The basal P-atoms give signals at -155 ppm and -190 ppm (5, 6, 7). The $^{31}$P-NMR shifts of $\mathrm{ClP_7[Si(SiMe_3)_3]_2}$, $\mathrm{BrP_7[Si(SiMe_3)_3]_2}$ and $\mathrm{IP_7[Si(SiMe_3)_3]}$ are summarized d in Table 2.

The presence of only seven or six groups of signals confirms that only the symmetric isomer was formed. This can be explained by the interaction of the two $\mathrm{Si(SiMe_3)_3}$ groups. Despite many attempts, crystals could not be obtained.

**Table 2: $^{31}$P-NMR shifts (ppm relative to $\mathrm{H_3PO_4}$ recorded in toluene) of $\mathrm{ClP_7[Si(SiMe_3)_3]_2}$, $\mathrm{BrP_7[Si(SiMe_3)_3]_2}$ and $\mathrm{IP_7[Si(SiMe_3)_3]_2}$.**

| | **$\mathrm{ClP_7[Si(SiMe_3)_3]_2}$** | **$\mathrm{BrP_7[Si(SiMe_3)_3]_2}$** | **$\mathrm{IP_7[Si(SiMe_3)_3]_2}$** |
|---|---|---|---|
| $\delta(P_1)$ | -97 | -97 | -98 |
| $\delta(P_2)$; $\delta(P_3)$ | -5; -57 | -1; -53 | -5; -40 |
| $\delta(P_4)$ | 175 | 145 | 86 |
| $\delta(P_5)$; $\delta(P_6)$; $\delta(P_7)$ | -148; -153; -192 | -152; -152; -188 | -155; -155; -179 |

### 3.7.3.1 Reaction of $\mathrm{XP_7[Si(SiMe_3)_3]_2}$ with Na/K alloy

In his thesis, Dr. V. Cappello reported on the synthesis of $\mathrm{{}^tBu(SiMe_3)_3SiP\text{-}P(SiMe_3)_3Si{}^tBu}$ from $\mathrm{ClP(SiMe_3)_3Si{}^tBu}$, joining two P-atoms using an halogenated silylphosphane and Na/K alloy. Starting form this result, $\mathrm{[Si(SiMe_3)_3]_2P_7\text{-}P_7[Si(SiMe_3)_3]_2}$ which consists of two $P_7$ cage linked by a PP-bond was expected to form in the reaction of $\mathrm{XP_7[Si(SiMe_3)_3]_2}$ with sodium/potassium alloy. The chlorinated compound $\mathrm{ClP_7[Si(SiMe_3)_3]_2}$ was synthesized and the Na/K alloy was added with a syringe to the toluene solution:

$$\mathrm{ClP_7[Si(SiMe_3)_3]_2} + \mathrm{Na/K} \not\longrightarrow \mathrm{[Si(SiMe_3)_3]_2P_7\text{-}P_7[Si(SiMe_3)_3]_2} + \mathrm{Na/KCl}$$

Interestingly, the formation of $\mathrm{[Si(SiMe_3)_3]_2P_7\text{-}P_7[Si(SiMe_3)_3]_2}$ was not observed but the $^{31}$P-NMR spectrum showed the typical shifts of $\mathrm{P_7[Si(SiMe_3)_3]_3}$. The $^{29}$Si-NMR spectrum also confirmed the presence of just $\mathrm{P_7[Si(SiMe_3)_3]_3}$.

### 3.7.3.2 Reaction of $XP_7[Si(SiMe_3)_3]_2$ with $Me_3SiOTf$

$$ClP_7[Si(SiMe_3)_3]_2 \ + \ Me_3SiOTf \ \nrightarrow \ P_7[Si(SiMe_3)_3]_2{}^+.[OTf]^- + Me_3SiCl$$

By reaction of trimethylsilyl trifluoromethylsulfonate $Me_3SiOTf$ with $ClP_7[Si(SiMe_3)_3]_2$ the formation of the first cationic heptaphosphane $R_2P_7^+$ was attempted. The chlorinated heptaphosphane $ClP_7(SiMe_3)_2$ was first synthesized and a toluene solution of $Me_3SiOTf$ was added dropwise at low temperature. A reaction occurred and the yellowish solution turned dark. According to the $^{31}$P-NMR spectrum, just degradation of the $P_7$-backbone occurred.

### 3.7.3.3 Reaction of $XP_7[Si(SiMe_3)_3]_2$ with $MP_7[Si(SiMe_3)_3]_2$

$$ClP_7[Si(SiMe_3)_3]_2 + K^+P_7[Si(SiMe_3)_3]_2{}^- \nrightarrow [Si(SiMe_3)_3]_2P_7\text{-}P_7[Si(SiMe_3)_3]_2 + KCl$$

As described in Section 2.2.1, one method to link two P-atoms is the addition of a halogenophosphane to a phosphanide. The chlorinated heptaphosphane $ClP_7[Si(SiMe_3)_3]_2$ and the potassium salt $[P_7(Si(SiMe_3)_3)_2]^-K^+$ were synthesized and the anion was added dropwise to $ClP_7(SiMe_3)_2$ at low temperature. Here again, the reaction led quantitatively to $P_7[Si(SiMe_3)_3]_3$.

## 3.8 Synthesis of hydrogenoheptaphosphanes

Trihydroheptaphosphane $P_7H_3$ was the first neutral polycyclic phosphane isolated in the pure state which was obtained by mild methanolysis of tris(trimethylsilyl)heptphosphane. [95]

$$P_7\,(SiMe_3)_3 \;+\; 3\,MeOH \xrightarrow{-40^\circ C} P_7\,H_3 \;+\; 3\,Me_3SiOMe$$

This compound was amorphous to X-rays and insoluble in many solvents. Synthesis of $P_7$-cages bearing hydrogen atoms $P_7R_2H$ and $P_7RH_2$ and their reactivity is one of the aim of this work.

### 3.8.1 Synthesis of $H_nP_7(SiMe_3)_{3-n}$

Starting form the results of Baudler, the partial direct methanolysis of $P_7(SiMe_3)_3$ appears as a good method to synthesize the cages $H_nP_7(SiMe_3)_{3-n}$. The reason for using this method is the very high reactivity of the P-$SiMe_3$ bond to alcohols or water:

$$P\text{—}SiMe_3 + HOR \rightarrow P\text{—}H + Me_3SiOR$$

$$2P\text{—}SiMe_3 + HOH \rightarrow 2P\text{—}H + Me_3SiOSiMe_3$$

In this attempt, we intended to develop a synthetic pathway leading to the hydrogenated heptaphosphane $HP_7(SiMe_3)_2$ which was expected to be a very useful synthon for many polyphosphorus compounds. Addition of methanol to a toluene solution of $P_7(SiMe_3)_3$ at very low temperature didn't lead to the expected $HP_7(SiMe_3)_2$. The reaction was very fast and the yellowish transparent solution turned to a deep yellow, with formation of yellowish insoluble material which settled at the bottom of the flask.

$$P_7\,(SiMe_3)_3 \;+\; 1\,R\text{-}OH \xrightarrow{-40^\circ C} HP_7\,(SiMe_3)_2 \;+\; 1\,Me_3SiOMe$$

Different polycyclic phosphanes as well as heptaphosphanes were present in solution, but the target compound $HP_7(SiMe_3)_2$could not be identified with reliability.

---

[95] Baudler, M.; Ternberger, H.; Faber, W.; Hahn, J.; *Z. Naturforsch.* **1979**, 34b, 1690.

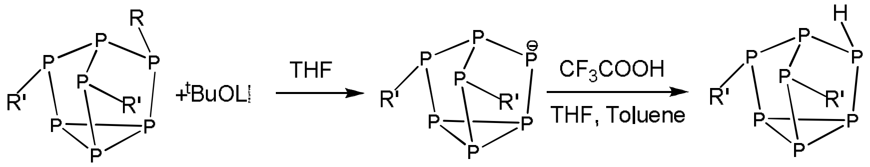
The analysis of the solution by NMR was quiet complicated due to the presence of a lot of signals. Obviously, a mixture of the $P_7$-cages $P_7H_3$, $SiMe_3P_7H_2$ and $(SiMe_3)_2P_7H$, unreacted $P_7(SiMe_3)_3$ as well as compounds resulting from a rearrangement of the $P_7$-backbone and degradation were formed. The analysis was also complicated by the possible presence of different isomers of the hydrogenated cages. Separation of any pure compound by fractional crystallisation was not successful. Similar results were observed using *tert*-butanol as reactant.

Due to the small size of the $SiMe_3$-substituent and its properties as very good leaving group, $P_7(SiMe_3)_3$ was not a valuable educt for the synthesis of stable partially hydrogenated heptaphosphanes $H_nP_7(SiMe_3)_{3-n}$.

### 3.8.2 Synthesis of $H_nP_7[Si(SiMe_3)_3]_{3-n}$

Due to the size of the hypersilyl group, the $Si(SiMe_3)_3$-P bond should be more shielded from the nucleophilic attack than the $SiMe_3$-P bond. Different methods which could lead to the target compounds $H_nP_7[Si(SiMe_3)_3]_{3-n}$ were explored.

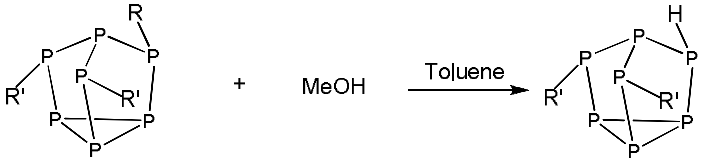
The first synthetic method started from the anion $M^+[P_7(Si(SiMe_3)_3)_2]^-$. It appeared that the action of the strong proton donor trifluoroacetic acid $CF_3CO_2H$ on the anion $Li^+[(Si(SiMe_3)_3)_2P_7]^-$ might be a good synthetic pathway to $HP_7[Si(SiMe_3)_3]_2$ (Scheme 62). The lithium anion was first synthesized in THF and a toluene solution of $CF_3CO_2H$ was added dropwise at low temperature. The reddish solution instantaneously turned light yellow. A $^{31}$P-NMR spectrum was performed (Figure 32) and the formation of $HP_7(Si(SiMe_3)_3)_2$ was confirmed.



**Scheme 62: Reaction pathway leading to $HP_7[Si(SiMe_3)_3]_2$ starting from the lithium salt $LiP_7(Si(SiMe_3)_3)_2$. R'= $Si(SiMe_3)_3$ R= $SiMe_3$**

The second method leading to $HP_7(Si(SiMe_3)_3)_2$ was the direct partial methanolysis of $[Si(SiMe_3)_3]_2P_7(SiMe_3)$. We presumed that only the $SiMe_3$-P bond should react with

MeOH. The use of other alcohols such as *t*-butanol or *iso*-propanol gave the same result.



**Scheme 63: Reaction pathway leading to $HP_7[Si(SiMe_3)_3]_2$ starting from the neutral cage $P_7$Rô$R_2$. Rô= $Si(SiMe_3)_3$ R= $SiMe_3$**

The spectrum shown below consists of five signals with relative intensities 1:2:1:2:1:

(a) -154 ppm and -170 ppm signals of the basal P-atoms ($P_b$);

(b) -106 ppm, signal of the apical P-atom ($P_a$);

(d) -5 ppm, signals of the P-atoms connected to the -$Si(SiMe_3)_3$ groups ($P_e$);

(e) 18 ppm, signals of the P-atom bearing the H atom ($P_e$).

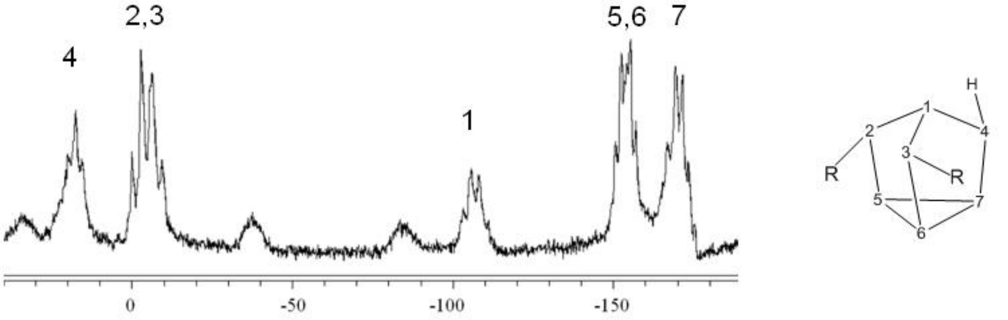


**Figure 32: $^{31}$P-NMR spectrum of $HP_7[Si(SiMe_3)_3]_2$ and structure of compound $HP_7[Si(SiMe_3)_3]_2$, the numbers replacing the P-atoms. R= $Si(SiMe_3)_3$.**

The product crystallised from n-hexane (Figure 33). It is the first structural example of a stable and neutral $P_7$-cage $R_2P_7H$.

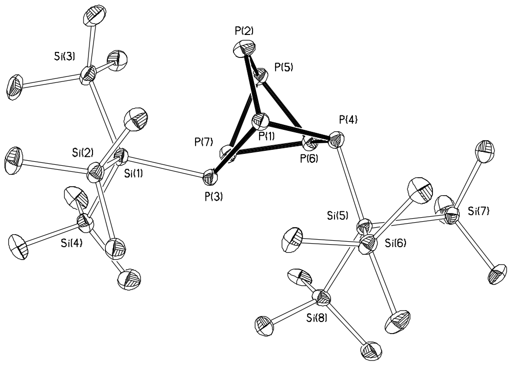


**Figure 33: Crystal structure of $HP_7[Si(SiMe_3)_3]_2$**

# 4 Experimental part

## 4.1 General procedure for syntheses

All syntheses and manipulations were carried out in flame-dry apparatuses under an inert atmosphere of dry nitrogen. Oxygen was removed by reduction with $H_2$ using a copper catalyst. $H_2O$ formed was then removed with $P_4O_{10}$. Many reactions were performed in a Glovebox.

Solvents were first dried over $Al_2O_3$ using a column purification system of Innovative Technology and then distilled from sodium, potassium, sodium-potassium alloy or $LiAlH_4$ to remove traces of moisture and oxygen.

18-crown-6, LiO$^t$Bu, NaO$^t$Bu and KO$^t$Bu were subjected to vacuum sublimation prior to use.

## 4.2 NMR Spectroscopy

NMR spectra were recorded on a Varian INOVA 300 ($^1$H: 299.95 MHz, $^{13}$C: 75.43 MHz, $^{29}$Si: 59.59 MHz, $^{31}$P: 121.42 MHz) or an INOVA 500 ($^1$H: 499.82 MHz, $^{13}$C: 125.89 MHz, $^{29}$Si: 99.30 MHz, $^{31}$P: 202.36 MHz) spectrometer. Shifts are reported in ppm down-field from TMS (tetramethylsilane) for $^1$H, $^{13}$C, $^{29}$Si and $H_3PO_4$ for $^{31}$P, and are referenced to solvent residual signal.

When spectra were measured directly from a reaction mixture in order to check the progression of a reaction, a $D_2O$ capillary was used as external lock.

To compensate for the low isotopic abundance of $^{29}$Si, the INEPT pulse sequence was often used.[109] To observe quarternary silicon atoms bonded to hydrogen or halogen DEPT and standard pulse sequences were used.

---

[109] (a) Morris, G. A.; Freeman R.; *J. Am. Chem. Soc.* **1979**, *101*, 760-762. (b) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877-879.; (c) Blinka, T. A.; Helmer, B. J.; West, R.; *Adv. Organomet. Chem.* **1984**, *23*, 193-218.

For the $^{31}P$-$^{31}P$ 2D-NMR spectra, typical COSY 45 or COSY 90 pulse sequence were used.

## 4.3 X-Ray structure determination

For X-ray structure analyses, the crystals were mounted onto the tip of glass fibers and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo K$\alpha$ radiation (0.71073 Å). The data were reduced to $F^2_o$ and corrected for absorption effects with SAINT[110] and SADABS,[111] respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).[112] If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30 % probability thermal ellipsoids and all hydrogen atoms were omitted for clarity. Unfortunately, the obtained crystal quality of some substances was poor. This fact is reflected by quite high R and low theta values.

## 4.4 Elemental analysis

Elemental analyses (C, H) were carried out on a Vario EL instrument by Heraeus Elementar.

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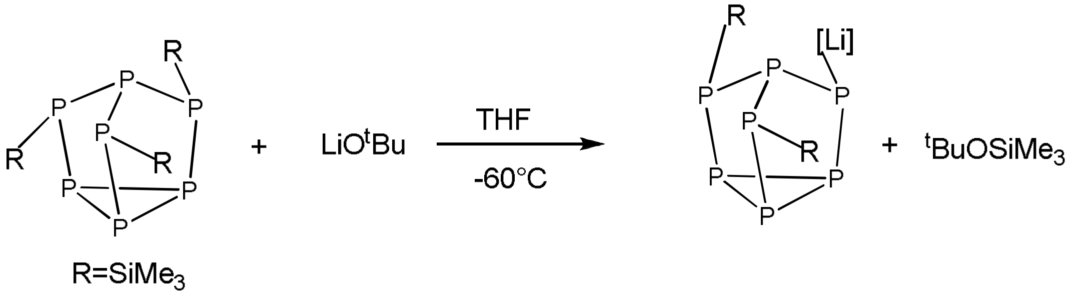
[110] *SAINTPLUS: Software Reference Manual*, Version 6.45; Bruker-AXS: Madison, WI, 1997-2003.

[111] Blessing, R. H.; *Acta Crystallogr. A* **1995**, *51*, 33-38.; *SADABS*, Version 2.1; Bruker AXS: Madison, WI, 1998.

[112] Sheldrick, G. M.; *SHELX97*, Programs for Crystal Structure Analysis (Release 97-2); Universität Göttingen: Göttingen (Germany), 1998.

## 4.5 Synthesis of new compounds

### 4.5.1 Synthesis of sym $[P_7(SiMe_3)_2]^-Li^+$



| | | | |
|---|---|---|---|
| $P_7SiMe_3$ | 1.00 g | 436.30 g.mol$^{-1}$ | 2.29 mmol |
| LiO$^t$Bu | 0.18 g | 80.05 g.mol$^{-1}$ | 2.29 mmol |

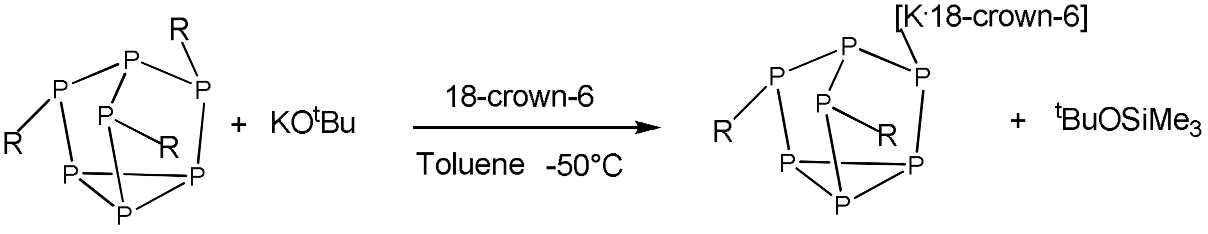
In a 100 mL two necked flask, $P_7TMS_3$ (1.00 g, 2.29 mmol) was dissolved in dry THF (20 mL). The solution was cooled to -50°C (cold methanol bath) and a solution of LiO$^t$Bu (0.18 g, 2.29 mmol) in dry THF (20 mL) was added dropwise under stirring over a period of 10 minutes. The colourless solution immediately turned yellow and was stirred at -50°C for a period of 1h. The reaction mixture was then allowed to warm up to room temperature. The solution then showed an intensely red colour. Crystals could not be obtained, neither at -30°C nor at -80°C.

$^1$H NMR (THF): δ = 0.3 (s)

$^{31}$P-NMR (THF): δ = -33.7 (m, 2P), -58.8 (m, 1P), -70.3 (m, 2P), -107.6 (m, 1P), -174.1 (m, 1P)

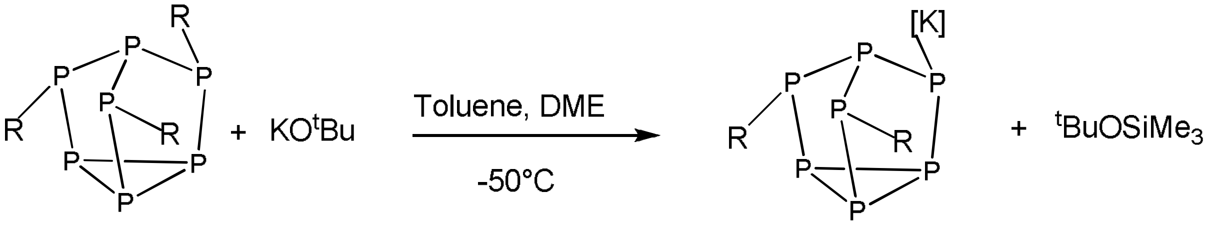
$^{29}$Si NMR (THF): δ = 3.5 (d,*Si*) $^1$J (SiP) < 12 Hz

### 4.5.2 Synthesis of asym $[P_7(SiMe_3)_2]^-K^+$



| | | | |
|---|---|---|---|
| $P_7SiMe_3$ | 1.50 g | 436.30 g.mol$^{-1}$ | 3.44 mmol |
| KO$^t$Bu | 0.38 g | 112.10 g.mol$^{-1}$ | 3.44 mmol |

In a 100 mL two necked flask, $P_7TMS_3$ (1.50 g, 3.44 mmol) was dissolved in a mixture of dry toluene and DME (25mL / 6mL). The solution was cooled down to -50°C and KO$^t$Bu (0.38 g, 3.44 mmol) was added with a spatula under stirring. The colourless solution turned intensely red immediately, and was stirred at -50°C for a period of 1h. The reaction mixture was then allowed to warm up to room temperature. All attempts to get crystals were unsuccessful.



| | | | |
|---|---|---|---|
| $P_7SiMe_3$ | 1.50 g | 436.30 g.mol$^{-1}$ | 3.44 mmol |
| KO$^t$Bu | 0.38 g | 112.21 g.mol$^{-1}$ | 3.44 mmol |
| 18-crown-6 | 0.91 g | 264.20 g.mol$^{-1}$ | 3.44 mmol |

In a 100 mL two necked flask, $P_7TMS_3$ (1.50 g, 3.44 mmol) was dissolved in a mixture of dry toluene and DME (20 mL / 10 mL). KO$^t$Bu (0.38 g, 3.44 mmol) was dissolved in dry DME (30mL) in a 100 mL dropping funnel and added dropwise at -50°C over a period of 20 min. The solution turned intensely red immediately. After 1 hour stirring at -50°C the temperature was allowed to rise to room temperature. Crystals could not be grown.

$^1$H NMR (Toluene): δ = 0.3 (s)

$^{31}$P-NMR (Toluene): δ = -17.1 (m, 1P), -23.7 (m, 1P), -70.7 (m, 1P), -88.8 (m, 1P), -179.5 (m, 1P), -192.1 (m, 2P)

$^{29}$Si NMR (Toluene): δ = 2.4 (d, *Si*Me$_3$) $^1$J (SiP) = 27.4 Hz

### 4.5.3 Synthesis of $[P_7(SiMe_3)_2]^-Na^+$

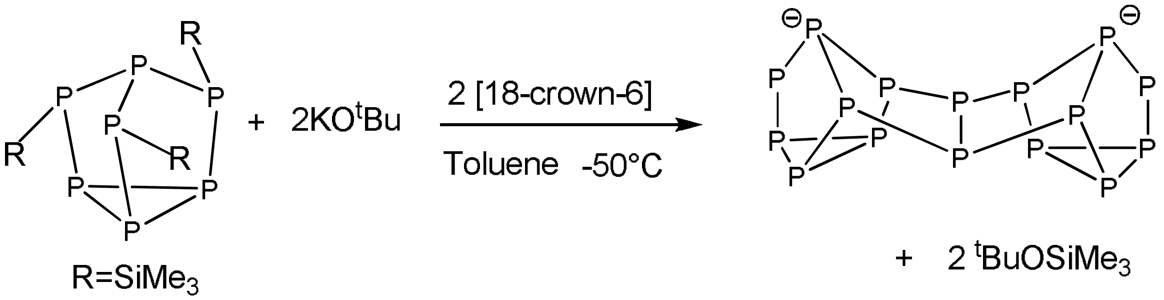
$$P_7(SiMe_3)_3 + NaO^tBu \longrightarrow [P_7(SiMe_3)_2]^-Na^+ + {}^tBuOSiMe_3$$

| | | | |
|---|---|---|---|
| $P_7SiMe_3$ | 1.00 g | 436.30 g.mol$^{-1}$ | 2.29 mmol |
| NaO$^t$Bu | 0.22 g | 96.11 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL two necked flask, $P_7TMS_3$ (1.00 g, 2.29 mmol) was dissolved in dry THF (20 mL). The solution was cooled to -50°C, and a solution of NaO$^t$Bu (0.22 g, 2.29 mmol) in dry THF (20 mL) was added dropwise over a period of 10 minutes. The colourless solution turned intensely red immediately, and was stirred at -50°C for a period of 1h. The temperature was then allowed to rise up to room temperature.The solution then showed an intensely red colour. The $^{31}$P-NMR spectrum showed that a mixture of symmetric and asymmetric anion had formed. Crystals could not be obtained, neither at -30°C nor at -80°C.

$^{31}$P-NMR (Toluene): δ = -22.3 (m), -34.2 (m), - 43.9 (m), -71.20 (m), -92.4 (m), -106.7 (m), -151.6 (m), -175.60 (m), -197.1 (m).

### 4.5.4 Synthesis of $[K^+]_2[P_{16}]^{2-}$



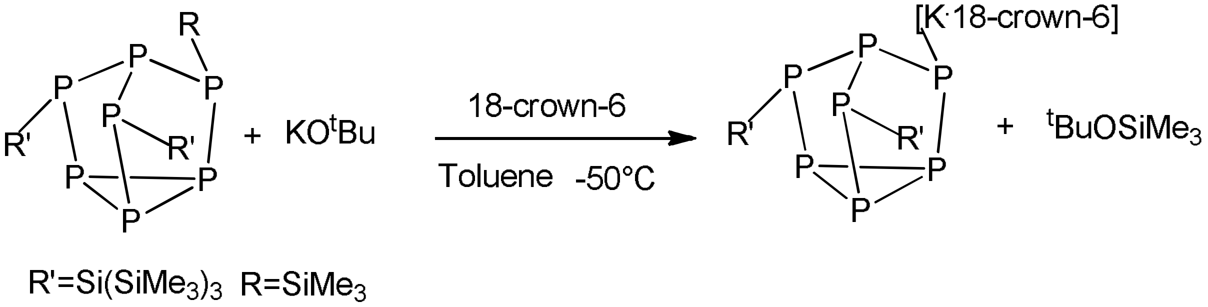
| | | | |
|---|---|---|---|
| $P_7SiMe_3$ | 1.50 g | 436.30 g.mol$^{-1}$ | 3.44 mmol |
| KO$^t$Bu | 0.76 g | 112.21 g.mol$^{-1}$ | 6.87 mmol |
| 18-crown-6 | 1.82 g | 264.22 g.mol$^{-1}$ | 6.87 mmol |

In a 100 mL two necked flask $P_7(SiMe_3)_3$ (1.50 g, 3.44 mmol) was dissolved in dry toluene (30 mL). The solution was cooled to -50°C. An excess of KO$^t$Bu (0.76 g, 6.87 mmol) and 18-crown-6 (1.82 g, 6.87 mmol) was dissolved in 30 mL dry toluene. The solution was added dropwise over a period of 20 min to the $P_7TMS_3$ solution cooled down to -50°C. The colourless solution turned intensely red immediately, and was stirred at -50°C for a period of 2h. The mixture was then allowed to warm up to room temperature. After one day, $[P_{16}]^{2-}$ had crystallised on the surface of the flask in form of dark crystals. The crystals were separated from the solution by decantation. They were soluble in THF.

Alternatively, $P_7TMS_3$ (1.00 g, 2.29 mmol) was dissolved in a mixture of dry toluene and DME (25 mL / 6 mL). The mixture was cooled to -50°C and an excess of KO$^t$Bu (0.51 g, 4.58 mmol) was added with a spatula. The colourless solution immediately turned intensely red, and was stirred at -50°C for a period of 2h. The mixture was then slowly warmed up to room temperature.

$^{31}$P-NMR (Toluene), δ: 60.2 (m, 4P), 39.7 (m, 2P), 6.9 (m, 2P), -34.41 (m, 2P), -133.2 (m, 2P), -172.0 (m, 4P).

### 4.5.5 Synthesis of $[P_7(Si(SiMe_3)_3)_2]^-K^+$



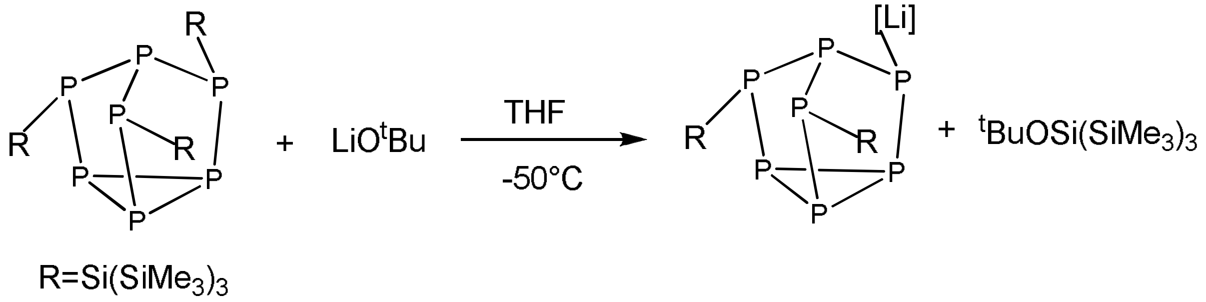
| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)]_2$ | 1.00 g | 791.36 g.mol$^{-1}$ | 1.26 mmol |
| KO$^t$Bu | 0.14 g | 112.21 g.mol$^{-1}$ | 1.26 mmol |
| 18-crown-6 | 0.33 g | 264.22 g.mol$^{-1}$ | 1.26 mmol |

In a 100 mL two necked flask, $SiMe_3P_7[Si(SiMe_3)_3]_2$ (1.00 g, 1.26 mmol) was dissolved in dry toluene (15 mL). The solution was cooled to -50°C, and a solution of KO$^t$Bu (0.14 g, 1.26 mmol) and 18-crown-6 (0.33 g, 1.26 mmol) in dry toluene (15 mL) was added dropwise over a period of 10 minutes. The colourless solution immediately turned red, and was stirred at -50°C for a period of 1h. The reaction mixture was then allowed to warm up to room temperature and insoluble by-products were separated from the solution by decantation. The anion was stable at room temperature for a couple of days and for weeks if kept at -80°C. Crystals suitable for X-rays analysis could be grown from toluene at -80°C.

$^{31}$P-NMR (Toluene): δ = -9.0 (m, 1P), -46.2 (m, 1P), -66.5 (m, 1P), -75.7 (m, 1P), -94.0 (m, 1P), -190.6 (m, 2P).

$^{29}$Si NMR (Toluene): δ = -11.9 ppm (*Si*Me$_3$),
δ = - 99.9 ppm, (d, *Si*(SiMe$_3$)) $^1$J (SiP) = 100 ± 5 Hz.

### 4.5.6 Synthesis of $[P_7(Si(SiMe_3)_3)_2]^-Li^+$ from $P_7[Si(SiMe_3)_3]_3$



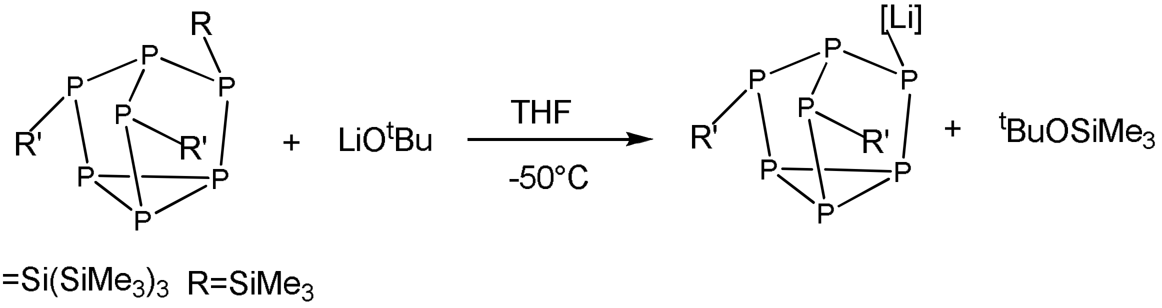
| | | | |
|---|---|---|---|
| $P_7[Si(SiMe_3)_3]_3$ | 0.50 g | 959.77 $g.mol^{-1}$ | 0.52 mmol |
| $LiO^tBu$ | 0.04 g | 80.05 $g.mol^{-1}$ | 0.52 mmol |

In a 100 mL two necked flask, $P_7[Si(SiMe_3)_3]_3$ (0.50 g, 0.52 mmol) was disolved in dry THF (15 mL). The solution was cooled to -50°C, and a solution of $LiO^tBu$ (0.04 g, 0.52 mmol) in dry THF (5 mL) was added dropwise over a period of 5 minutes. The colourless solution immediately turned yellow and was stirred at -50°C for a period of 1h. The temperature was then allowed to raise to room temperature, and the colour of the solution had changed to pale orange. The solution was warmed up to 50°C and stirred for 10 days. The colour of the solution slowly changed to dark red. All attempts to grow crystals failed.

$^{31}$P-NMR (THF): δ = -10.5 (m, 1P), -47.0 (m, 1P), -69.8 (m, 2P 2 signals overlapped), -95.0 (m, 1P), -189.6 (m, 2P).

$^{29}$Si-NMR (THF): δ = -9.9 ppm (*Si*$Me_3$),
δ = -99.8 ppm (d, *Si*($SiMe_3$)), $^1J$ (SiP) = 100 ± 5 Hz.

### 4.5.7 Synthesis of $[P_7(Si(SiMe_3)_3)_2]^-Li^+$ from $SiMe_3P_7[Si(SiMe_3)_3]_2$



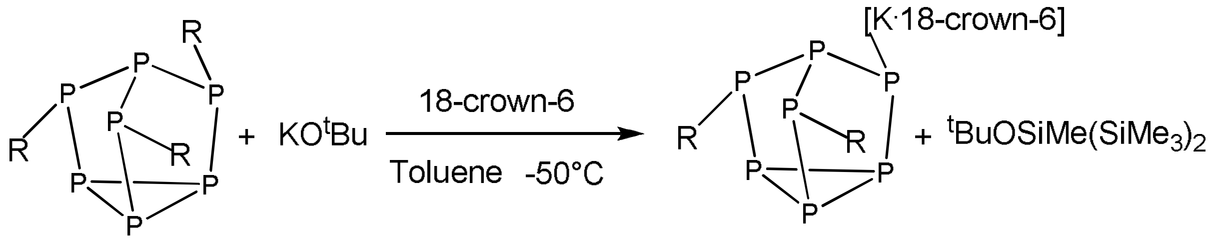
| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 1.00 g | 791.36 g.mol$^{-1}$ | 1.26 mmol |
| LiO$^t$Bu | 0.11 g | 80.05 g.mol$^{-1}$ | 1.26 mmol |

In a 100 mL two necked flask, $SiMe_3P_7[Si(SiMe_3)_3]_2$ (1.00 g, 1.26 mmol) was dissolved in dry toluene (15 mL). The solution was cooled to -50°C, and a solution of LiO$^t$Bu (0.11 g, 1.26 mmol) in dry THF (5 mL) was added dropwise over a period of 5 minutes. The colourless solution immediately turned red and was stirred at -50°C for a period of 1h. The solution was then allowed to warm up to room temperature, and the salts were separated from the solution by decantation. Crystals could not be obtained, neither at -30°C nor at -80°C.

$^{31}$P-NMR (THF): δ = -10.5 (m, 1P), -47.0 (m, 1P), -69.8 (m, 2P 2 signals overlapped), -95.0 (m, 1P), -189.6 (m, 2P).

$^{29}$Si-NMR (THF): δ = -9.9 ppm (*Si*Me$_3$),
δ = -99.8 ppm (d, *Si*(SiMe$_3$)), $^1$J (SiP) = 100 ± 5 Hz.

### 4.5.8 Synthesis of $[P_7(SiMe(SiMe_3)_2)_2]^-K^+$



R=$SiMe(SiMe_3)_2$

| | | | |
|---|---|---|---|
| $P_7[SiMe(SiMe_3)_2]_3$ | 0.50 g | 785.31 $g.mol^{-1}$ | 0.64 mmol |
| $KO^tBu$ | 0.07 g | 112.21 $g.mol^{-1}$ | 0.64 mmol |
| 18-crown-6 | 0.17 g | 264.22 $g.mol^{-1}$ | 0.64 mmol |

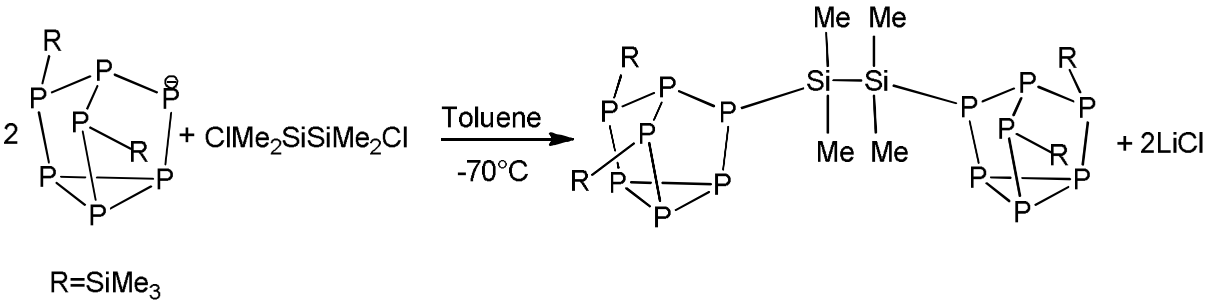
In a 100 mL two necked flask, $P_7[SiMe(SiMe_3)_2]_3$ (0.50 g, 0.64 mmol) was dissolved in dry toluene. The solution was cooled to -50°C and a solution of $KO^tBu$ (0.07 g, 0.64 mmol) and 18-crown-6 (0.17 g, 0.64 mmol) in dry toluene (30 mL) was added dropwise over a period of 20 min under strong stirring. The solution slowly turned red. After 2 hours at -50°C, the reaction mixture was allowed to warm up to room temperature. The solution was stirred at room temperature for 6 hours and turned into a deep red colour, and was then separated from insoluble by-products by decantation. Despite many attempts, crystals could not be obtained.

$^{31}$P-NMR (THF): δ = -18.9 (m, 1P), -36.3 (m, 1P), -58.9 (m, 2P), -95.6 (m, 1P), -190.4 (m, 2P).

$^{29}$Si-NMR (THF): δ = -8.5 ppm (s, *Si*$Me_3$),

δ = -49.0 ppm (d, *Si*Me) $^1J$ (SiP) = 89 Hz ± 5 Hz.

### 4.5.9 Synthesis of $(Me_3Si)_2P_7Si_2Me_4P_7(SiMe_3)_2$ from $[P_7(SiMe_3)_2]^-Li^+$ and $ClSiMe_2SiMe_2Cl$



| | | | |
|---|---|---|---|
| $[P_7(SiMe_3)_2]^-Li^+$ | | | 2.29 mmol |
| $ClSiMe_2SiMe_2Cl$ | 0.22 g | 283.40 g.mol$^{-1}$ | 1.17 mmol |

In a 100 mL two necked flask, $ClSiMe_2SiMe_2Cl$ (0.22 g, 1.17 mmol) was dissolved in dry toluene (10 mL). The solution was cooled to -70°C, and a solution of $Li^+[P_7(SiMe_3)_2]^-$ (2.29 mmol, prepared from 1.00 g of $P_7(SiMe_3)_3$ and 0.18 g $LiO^tBu$) in dry THF (40 mL) was added dropwise over a period of 20 minutes under strong stirring. The reddish solution was stirred at -70 °C for a period of 2h. The colour of the solution changed into light yellow. The mixture was very slowly warmed up to room temperature. The solution was left at room temperature for 4 days, and salts precipitated. The solution was separated from the salts by decantation. The product crystallised from n-hexane at -80°C in the form of yellow crystals too small for X-ray analysis. Yield: 0.22 g (± 25%).

$^1$H NMR ($C_6D_6$): δ = 0.27 (d, 36H), 0.12 (d, 12H).

$^{31}$P-NMR ($C_6D_6$): δ = 25.4 (m, 2P), 5.2 (m, 4P), -61.5 (m, 2P), -161.8 (m, 2P), -154.5 (m, 2P), -146.3 (m, 2P).

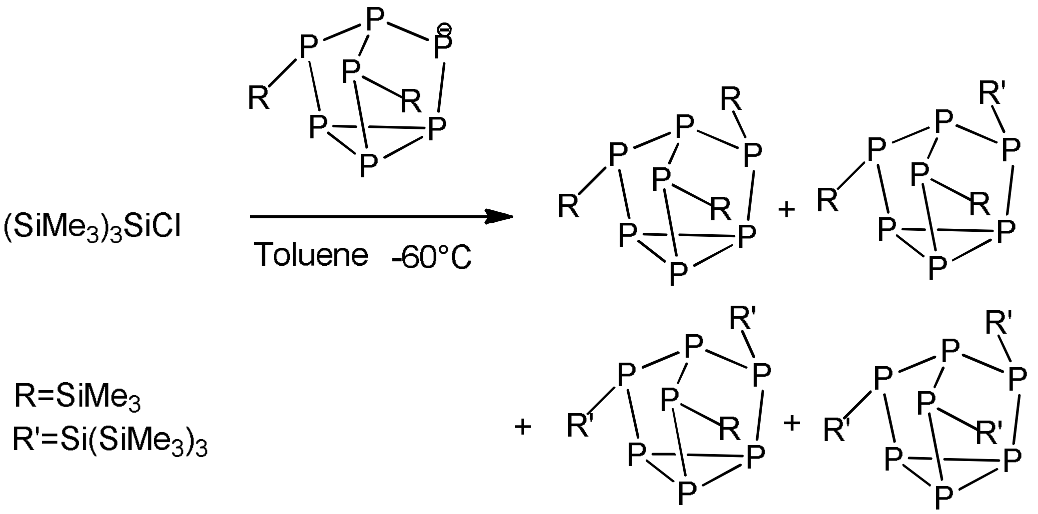
$^{29}$Si NMR ($C_6D_6$): δ = 2.4 (d, 4Si), $^1J$ (SiP) ≈ 27 Hz,
δ = -26.5 (d, 2Si), $^1J$ (SiP) ≈ 47 Hz.

Elemental analysis:

$C_{16}H_{48}Si_6P_{14}$ (842,70): calculated. C 22.8, H 5.74; found C 22.37, H 5.44.

### 4.5.10 Derivatization of $[P_7(SiMe_3)_2]^-K^+$

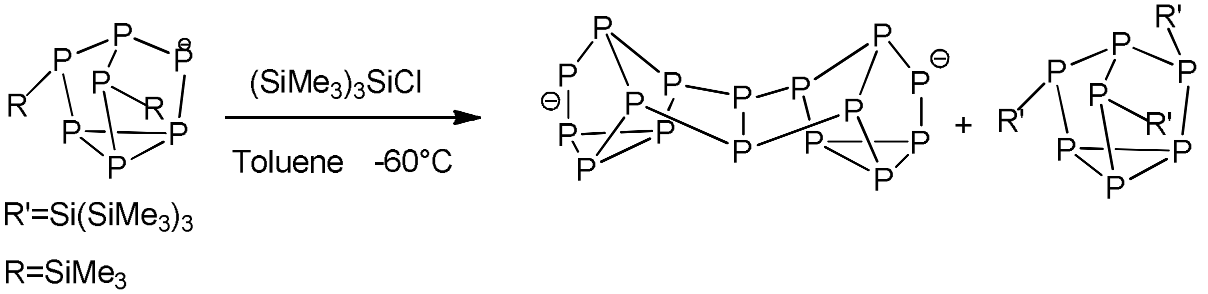
#### 4.5.10.1 Reaction of $K^+[P_7(SiMe_3)_2]^-$ with $(SiMe_3)_3SiCl$



| | | | |
|---|---|---|---|
| $[P_7(SiMe_3)_2]^-K^+$ | | | 2.29 mmol |
| $(SiMe_3)_3SiCl$ | 0.65 g | 283.40 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL two necked flask, $(SiMe_3)_3SiCl$ (0.65 g, 2.29 mmol) was dissolved in dry toluene (20 mL). The solution was cooled to -60°C, and a solution of $K^+[P_7(SiMe_3)_2]^-$ (2.29 mmol prepared from 1.00 g of $P_7(SiMe_3)_3$ and 0.25g of KO$^t$Bu) in a mixture of dry toluene and DME (30 mL / 8 mL) was added dropwise over a period of 20 minutes. The solution turned yellowish. After stirring for 2 hours, the solution was allowed to come to room temperature and was then separated from the salts by decantation. The solvent was removed i.v. and a residue of unreacted $(SiMe_3)_3SiCl$ was removed by sublimation at 50 °C under vacuum. The residue was dissolved in dry methylcyclohexane (40mL) and cooled to -80°C. Crystals obtained were a mixture of at least three products: $(SiMe_3)_3SiP_7(SiMe_3)_2$, $((SiMe_3)_3Si)_2P_7(SiMe_3)$, $((SiMe_3)_3Si)_3P_7$.

The reaction with $Li^+[P_7(SiMe_3)_2]^-$ led to the same result.



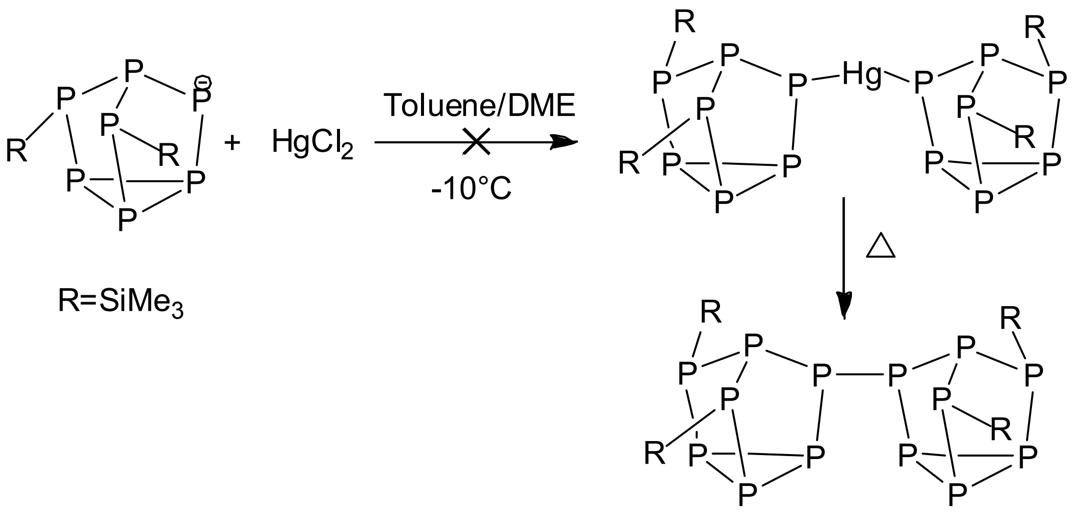
| | | | |
|---|---|---|---|
| $[P_7(SiMe_3)_2]^-K^+$ | | | 2.29 mmol |
| $(SiMe_3)_3SiCl$ | 0.65 g | 283.40 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL two necked flask, $K^+[P_7(SiMe_3)_2]^-$ (2.29 mmol prepared from 1.00g of $P_7(SiMe_3)_3$ and 0.25g of $KO^tBu$) was synthesised in a mixture of dry toluene and DME (30 mL / 8 mL). The solution was cooled to -60°C, and $(SiMe_3)_3SiCl$ (0.65 g, 2.29 mmol) dissolved in dry toluene (20 mL) was added dropwise over a period of 20 minutes under strong stirring. The colour of the solution slowly changed to a light yellow. After 2 hours at -50°C, the solution was warmed to room temperature. The stirring was switched off and the solution was left at room temperature. After a couple of hours, dark crystals had precipitated on the wall of the flask. The yellow solution was separated from the dark crystals by decantation. Crystals were dissolved in dry THF and $^{31}P$-NMR was performed for both solutions. The THF solution contained $[P_{16}]^{2-}$, the mixture of toluene and DME contained $P_7[Si(SiMe_3)_3]_3$.

$^{31}P$-NMR (THF): δ = 60.2 (m, 4P), 39.7 (m, 2P), 6.9 (m, 2P), -34.4 (m, 2P), -133.2 (m, 2P), -172.0 (m, 4P).

$^{31}P$-NMR (Toluene, DME): δ = -1.9 ppm (m, 3P), δ = -100.8 ppm (m, 1P), δ = -165.6 ppm (m, 3P).

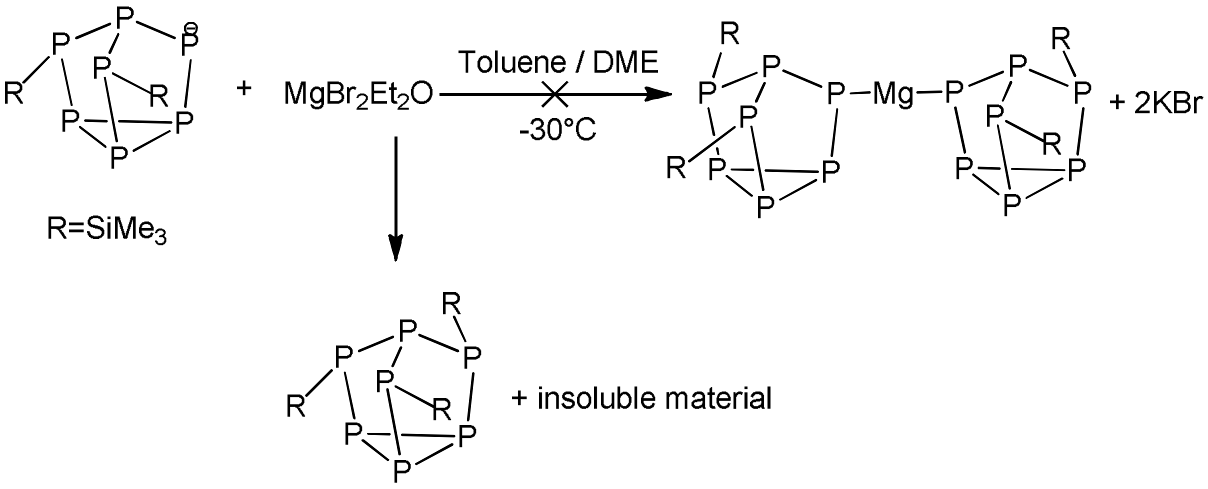
### 4.5.10.2 Reaction with $HgCl_2$



| | | | |
|---|---|---|---|
| $[P_7(SiMe_3)_2]^-K^+$ | | | 2.29 mmol |
| Hg | 0.62 g | 271.49 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL two necked flask, $[P_7(SiMe_3)_2]^-K^+$ (2.29 mmol prepared from 1.00 g of $P_7(SiMe_3)_3$ and 0.25g of KO$^t$Bu) was synthesised in a mixture of dry toluene and DME (30 mL / 5 mL). The solution was cooled to -10°C and $HgCl_2$ (0.62 g, 2.29 mmol) was added under strong stirring with a spatula. The reddish solution immediately turned dark and was stirred at -10°C for a period of 4 hours. The mixture was allowed to slowly warm up to room temperature. After a few hours at room temperature, dark oily salts had settled on the bottom of the flask. According to the $^{31}$P-NMR spectrum, just decomposition of the starting material $P_7(SiMe_3)_3$ was observed.

### 4.5.10.3 Reaction with $MgBr_2Et_2O$

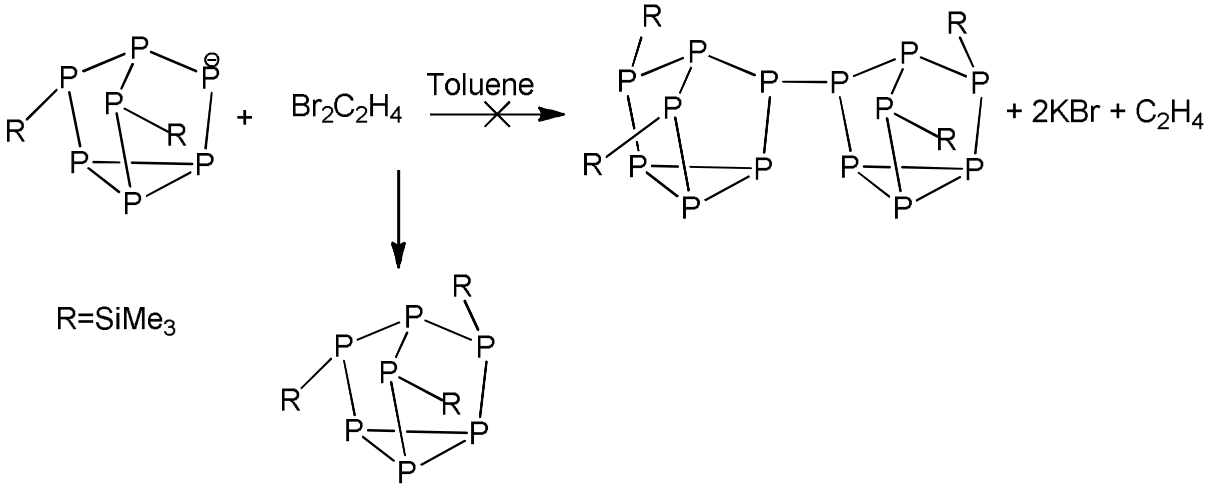


| | | | |
|---|---|---|---|
| $[P_7(SiMe_3)_2]^-K^+$ | | | 2.29 mmol |
| $MgBr_2Et_2O$ | 0.88 g | 258.23 g.mol$^{-1}$ | 3.39 mmol |

In a 100 mL two necked flask, $[P_7(SiMe_3)_2]^-K^+$ (2.29 mmol prepared from 1.00 g of $P_7(SiMe_3)_3$ and 0.25g of KO$^t$Bu) was synthesised in a mixture of dry toluene and DME (100mL / 15mL). The solution was cooled to -30°C and an excess (≈ 10%) of $MgBr_2Et_2O$ (0.88 g, 3.39 mmol) was added with a spatula. The reddish solution slowly turned dark and was stirred at -30°C for a period of 2 hours. The mixture was then allowed to warm up to room temperature. After a few hours, a dark precipitate had settled on the bottom of the flask. The solution was decanted. In the $^{31}$P-NMR spectrum, the typical signals of $P_7(SiMe_3)_3$ were observed. The precipitate was completely insoluble in toluene, THF, DME, n-hexane or heptane.

The same result was obtained starting from $[P_7(SiMe_3)_2]^-Li^+$.

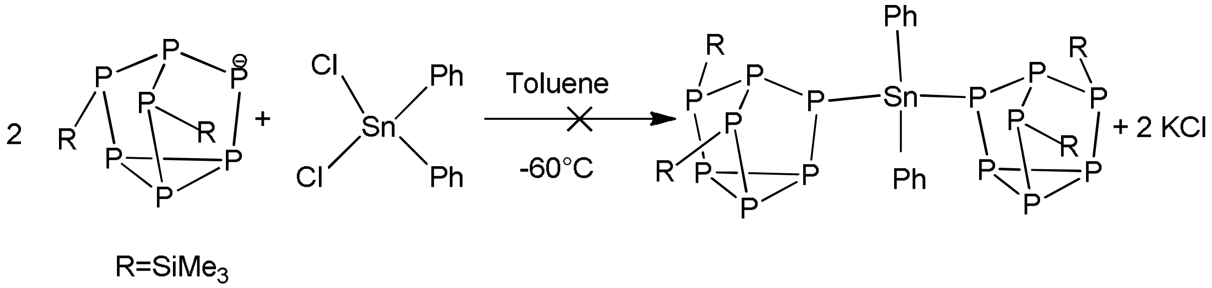
### 4.5.10.4 Reaction with $BrCH_2CH_2Br$



| | | | |
|---|---|---|---|
| $[P_7(SiMe_3)_2]^-K^+$ | | | 2.29 mmol |
| $Br_2C_2H_4$ | 0.22 g | 187.86 g.mol$^{-1}$ | 1.15 mmol |

In a 100 mL two necked flask, $[P_7(SiMe_3)_2]^-K^+$ (2.29 mmol prepared from 1.00 g of $P_7(SiMe_3)_3$ and 0.25g of KO$^t$Bu) was synthesised in a mixture of dry toluene and DME (16 mL / 4 mL). The solution was cooled to -50°C, and a solution of $BrCH_2CH_2Br$ (0.22 g, 1.15 mmol) in dry toluene (30 mL) was added dropwise over a period of 25 min. The reddish solution slowly turned dark and was stirred at -50°C for a period of 2 hours. The mixture was then slowly allowed to warm up to room temperature and the salts were separated from the solution by decantation. A $^{31}$P-NMR spectrum of the solution showed just the typical signals of $P_7(SiMe_3)_3$.

### 4.5.10.5 Reaction with $Cl_2SnPh_2$

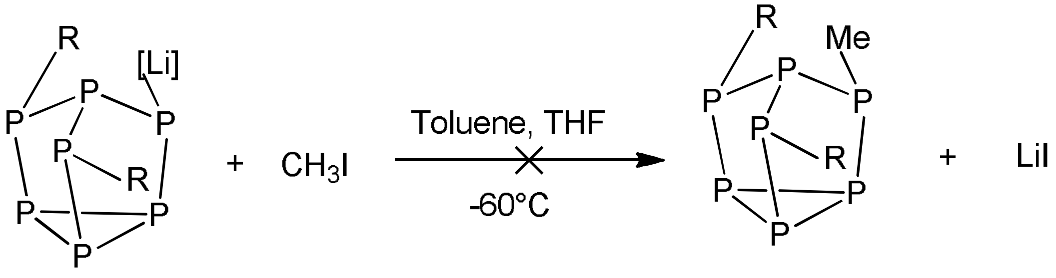


| | | | |
|---|---|---|---|
| $[P_7(SiMe_3)_2]^-K^+$ | | | 2.29 mmol |
| $Cl_2SnPh_2$ | 0.40 g | 343.80 g.mol$^{-1}$ | 1.15 mmol |

In a 100 mL two necked flask, $[P_7(SiMe_3)_2]^-K^+$ (2.29 mmol prepared from 1.00 g of $P_7(SiMe_3)_3$ and 0.25g of KO$^t$Bu) was synthesised in dry toluene. A solution of $Ph_2SnCl_2$ (0.40 g, 1.15 mmol) in dry toluene (20 mL) was added dropwise at -50°C over a period of 25 min. The reddish solution turned yellow and was stirred at -50°C for a period of 2 hours. The mixture was then allowed to warm up to room temperature, and the solution then showed a dark colour. After 4 hours, a dark precipitate (insoluble in THF) had settled on the bottom of flask. A $^{31}$P-NMR spectrum of the toluene solution showed the complete decomposition of the starting material.

## 4.5.11 Derivatization of $[P_7(SiMe_3)_2]^-Li^+$

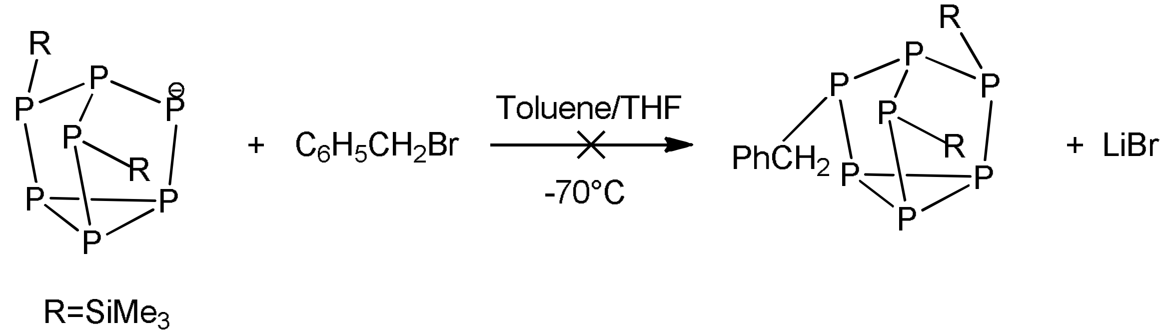
### 4.5.11.1 Reaction with $CH_3I$



| | | | |
|---|---|---|---|
| $[P_7(SiMe_3)_2]^-Li^+$ | | | 2.29 mmol |
| $CH_3I$ | 0.32 g | 141.93 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL two necked flask, $[P_7(SiMe_3)_2]^-Li^+$ (2.29 mmol prepared from 1.00 g of $P_7(SiMe_3)_3$ and 0.18 g of LiO$^t$Bu) was synthesised in 40 mL dry THF. The formation of $[P_7(SiMe_3)_2]^-Li^+$ was controlled by NMR spectroscopy. A solution of $CH_3I$ (0.32 g, 2.29 mmol) in dry toluene (20 mL) was added dropwise at -60°C over a period of 25 min. The reddish solution turned yellow and was stirred at -60°C for a period of 2 hours. The mixture was then allowed to come to room temperature. The solution then showed a yellow colour. The solvent was removed in vacuum and 20 mL of dry n-hexane was added. A $^{31}$P-NMR spectrum showed the complete decomposition of the $P_7$-cage.

### 4.5.11.2 Reaction with $PhCH_2Br$



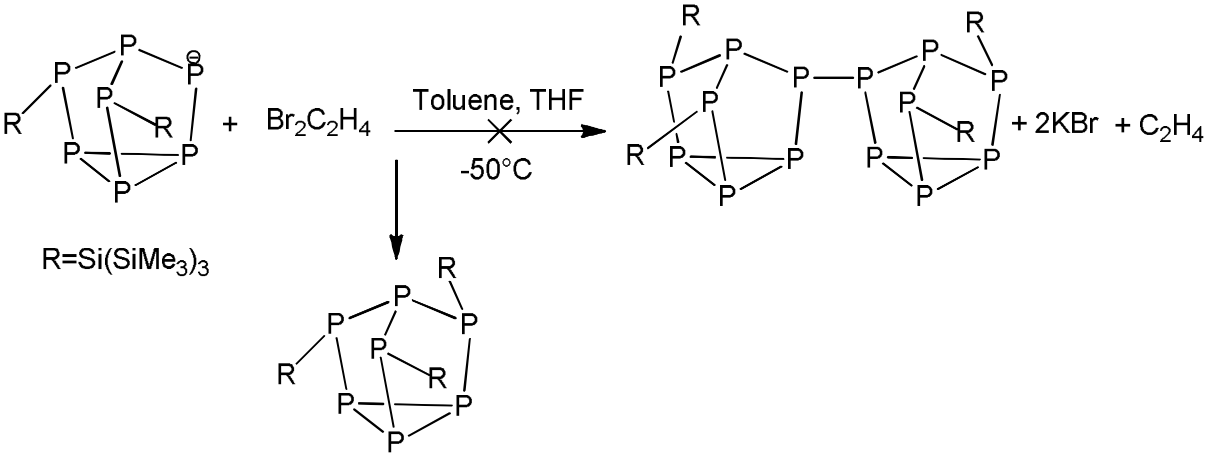
| | | | |
|---|---|---|---|
| $[P_7(SiMe_3)_2]^-Li^+$ | | | 2.29 mmol |
| $PhCH_2Br$ | 0.39 g | 171.03 g.mol$^{-1}$ | 2.29 mmol |

In a 150 mL two necked flask, $PhCH_2Br$ (0.39 g, 2.29 mmol) was dissolved in dry toluene (60mL). $Li^+[P_7(SiMe_3)_2]^-$ (2.29 mmol prepared from 1.00 g of $P_7(SiMe_3)_3$ and 0.18 g of $LiO^tBu$) was synthesized in dry THF, and was added dropwise at -70°C to the toluene solution over a period 20 min. The reddish solution turned yellow and was stirred at -50°C for a period of 2 hours. The solution then showed a dark brown colour. The mixture was then allowed to warm up to room temperature. According to the $^{31}$P-NMR spectrum, a reaction had occurred which did not give the desired product. A mixture of several polyphosphanes such as $[PhCH_2P_7SiMe_3)]^-$ or $[P_7(SiMe_3)_2]^-$ was present in solution.

When an excess of $PhCH_2Br$ (50 %, 0.20g) was added with a syringe, complete decomposition of the cage was observed.

## 4.5.12 Derivatization of $[P_7[Si(SiMe_3)_3]_2]^-$

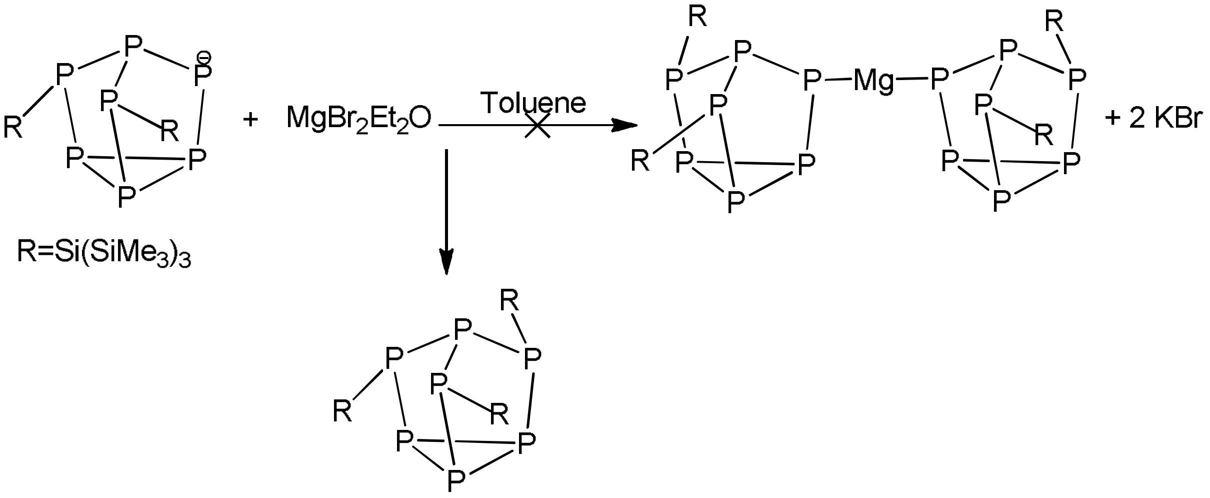
### 4.5.12.1 Reaction with $Br_2C_2H_4$



| | | | |
|---|---|---|---|
| $[P_7(Si(SiMe_3)_3)_2]^-Li^+$ | | | 1.26 mmol |
| $Br_2C_2H_4$ | 0.12 g | 187.86 g.mol$^{-1}$ | 0.63 mmol |

In a 100 mL two necked flask, $[P_7[Si(SiMe_3)_3]_2]^-Li^+$ (1.26 mmol prepared from 1.00 g of $SiMe_3P_7[Si(SiMe_3)_3]_2$ and 0.11 g LiO$^t$Bu) was synthesised in dry THF (20 mL). The solution was cooled to -50°C and $BrCH_2CH_2Br$ (0.12 g, 0.63 mmol) dissolved in dry toluene (10mL) was added dropwise over a period of 15 min. The reddish solution turned dark immediately, and was stirred at -50°C for a period of 1 hour. The mixture was then allowed to warm up to room temperature. The solution was separated from the salts by decantation. A $^{31}$P-NMR spectrum of the solution was recorded which showed just the typical signals of $P_7[Si(SiMe_3)_3]_3$.

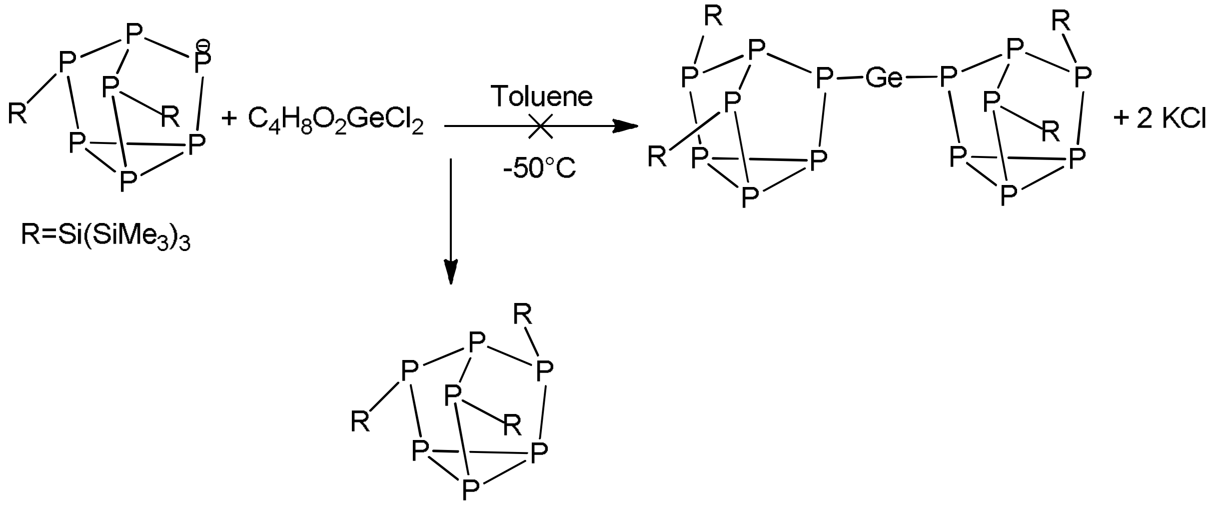
#### 4.5.12.2 Reaction with $MgBr_2Et_2O$



| | | | |
|---|---|---|---|
| $[P_7(Si(SiMe_3)_3)_2]^-K^+$ | | | 1.27 mmol |
| $MgBr_2Et_2O$ | 0.49 g | 258.23 g.mol$^{-1}$ | 1.89 mmol |

In a 100 mL two necked flask, $[P_7(Si(SiMe_3)_3)_2]^-K^+$ (1.27 mmol prepared from 1.00 g of $SiMe_3P_7[Si(SiMe_3)_3]_2$ and 0.14 g of KO$^t$Bu and 0.33 g of 18-crown-6) was synthesised in dry toluene (30 mL). The solution was cooled to -30°C and an excess (≈10%) of $MgBr_2Et_2O$ (0.49 g, 1.89 mmol) was added with a spatula under strong stirring. The reddish solution turned dark slowly and was stirred at -30°C for a period of 2 hours. The mixture was then allowed to warm up to room temperature. After a few hours, a dark precipitate had settled on the bottom of the flask. The solution was decanted from the precipitate. In the $^{31}$P-NMR spectrum of the solution, typical signals of $P_7[Si(SiMe_3)_3]_3$ were observed. The precipitate could not be dissolved in toluene, THF, DME, n-hexane or heptane.

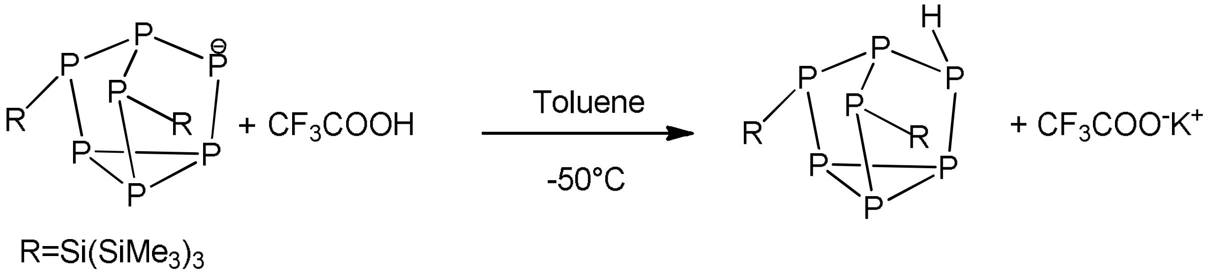
### 4.5.12.3 Reaction with $GeCl_2$



|  |  |  |  |
|---|---|---|---|
| $[P_7(Si(SiMe_3)_3)_2]^-K^+$ |  |  | 1.27 mmol |
| $C_4H_8O_2GeCl_2$ | 0.81 g | 231.62 g.mol$^{-1}$ | 3.51 mmol |

In a 100 mL two necked flask, $[P_7(Si(SiMe_3)_3)_2]^-K^+$ (1.27 mmol prepared from 1.00 g of $SiMe_3P_7[Si(SiMe_3)_3]_2$ and 0.14 g of KO$^t$Bu and 0.33 g of 18-crown-6) was synthesised in dry toluene (30 mL). In a dropping funnel, $GeCl_2$.dioxane (0.81 g, 3.51 mmol) was dissolved in 20 mL dry toluene. The solution of the anion was cooled to -50°C and the toluene solution of germanium dichloride was added dropwise over a period of 20 min. The mixture was stirred for 2 hours and was then allowed to warm up to room temperature. After a few hours, the reddish solution had turned pale yellow, and an insoluble precipitate settled on the bottom of the flask. The solution was decanted and kept at -80°C. In the $^{31}$P-NMR spectrum of the solution, just the typical signals of $P_7[Si(SiMe_3)_3]_3$ were observed.

### 4.5.12.4 Reaction with $CF_3COOH$



| | | | |
|---|---|---|---|
| $[P_7(Si(SiMe_3)_3)_2]^-K^+$ | | | 1.27 mmol |
| $CF_3COOH$ | 0.14 g | 114.03 g.mol$^{-1}$ | 1.27 mmol |

In a 100 mL two necked flask, $[P_7(Si(SiMe_3)_3)_2]^-K^+$ (1.27 mmol prepared from 1.00 g of $SiMe_3P_7[Si(SiMe_3)_3]_2$ and 0.14 g of $KO^tBu$ and 0.33 g of 18-crown-6) was synthesised in dry toluene (30 mL) and transferred into a dropping funnel. $CF_3COOH$ (0.14 g, 1.27 mmol) was dissolved in 10 mL toluene and the solution was cooled to -50°C. The toluene solution of anion was added dropwise over a period of 20 min, and the mixture was stirred for 2 hours. The mixture was then allowed to warm up to room temperature. The first reddish solution turned pale yellow, and a yellow precipitate settled on the bottom of the flask. Crystals suitable for X-rays analysis could be grown from toluene at -80°C.

Elemental analysis $C_{18}H_{55}Si_8P_7$ (713.13), found./calc: C: 30.72/30.32%, H: 7.24/7.77%.

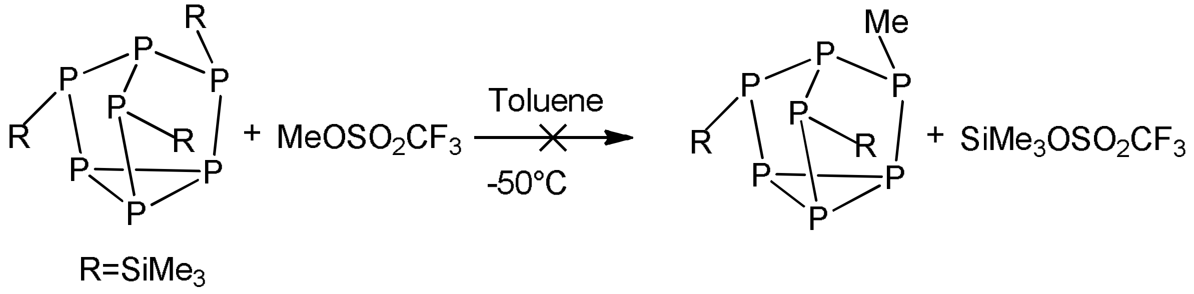
$^1$H-NMR ($C_6D_6$): $\delta$ = 0.4 (9H, SiMe$_3$), $\delta$ = 0.40 (9H, SiMe$_3$), $\delta$ = 3.1 (1H, $^1J$(PH) = 191 Hz).

$^{31}$P-NMR ($C_6D_6$): $\delta$ = 15.7 (t, 1P), -7.7 (m, 2P), -109.6 (m, 1P), -156.2 (m, 2P), -173.1 (m, 1P).

$^{29}$Si-NMR ($C_6D_6$): $\delta$ = -8.9 ppm (*Si*Me$_3$),
$\delta$ = -93.9 ppm (d, *Si*(SiMe$_3$)$_3$) $^1J$ (SiP) ≈ 82 Hz
$\delta$ = -95.2 ppm (d, *Si*(SiMe$_3$)$_3$) $^1J$ (SiP) ≈ 90 Hz

### 4.5.13 Derivatization of $P_7(SiMe_3)_3$

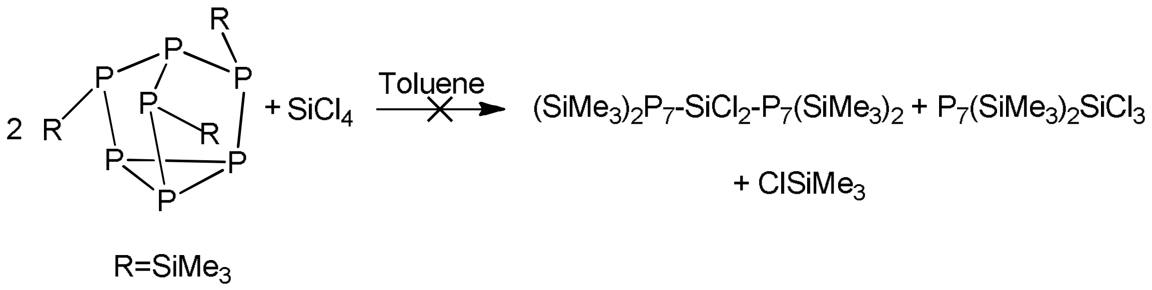
#### 4.5.13.1 Reaction with $MeOSO_2CF_3$



| | | | |
|---|---|---|---|
| $P_7SiMe_3$ | 1.00 g | 436.38 g.mol$^{-1}$ | 2.29 mmol |
| $MeOSO_2CF_3$ | 0.37 g | 161.10 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL two necked flask, $P_7(SiMe_3)_3$ (1.00g, 2.29 mmol) was dissolved in dry toluene (40 mL) and cooled down to -50°C. A solution of dry $MeOSO_2CF_3$ (0.37g, 2.29 mmol) was added with a syringe (Eppendorf Varipette) to the toluene solution under strong stirring. The light yellowish solution was stirred for 10 days at room temperature. According to the $^{31}$P-NMR spectrum, no reaction could be observed.

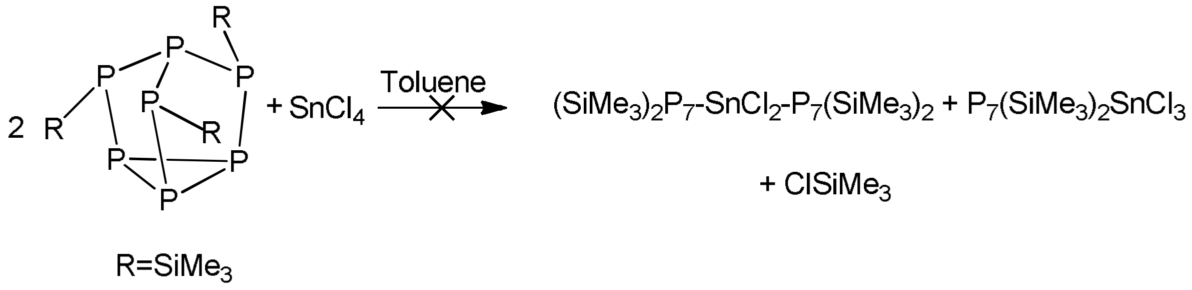
### 4.5.13.2 Reaction with $SiCl_4$



| | | | |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 0.50 g | 436.38 $g.mol^{-1}$ | 1.14 mmol |
| $SiCl_4$ | 0.24 g | 169.90 $g.mol^{-1}$ | 1.14 mmol |

In a vial, $P_7(SiMe_3)_3$ (0.5g, 1.14 mmol) was dissolved in dry toluene (40 mL). A solution of dry $SiCl_4$ (0.24 g, 1.14 mmol) was added with a syringe (Eppendorf Varipette) under strong stirring. The light yellowish solution was stirred for 2 days. According to the $^{31}$P-NMR spectrum, the complete degradation of $P_7(SiMe_3)_3$ was observed.

### 4.5.13.3 Reaction with $SnCl_4$

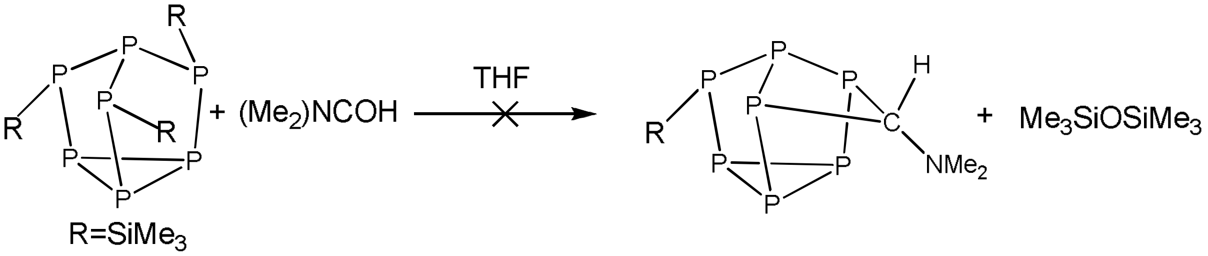


| | | | |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 0.50 g | 436.38 $g.mol^{-1}$ | 1.14 mmol |
| $SnCl_4$ | 0.38 g | 260.50 $g.mol^{-1}$ | 1.14 mmol |

In a vial $P_7(SiMe_3)_3$ (0.50 g, 1.14 mmol) was dissolved in dry toluene (40 mL. A solution of dry $SnCl_4$ (0.24 g, 1.14 mmol) was added with a syringe (Eppendorf

Varipette) under stirring. The light yellowish solution was stirred for 1 day. According to the $^{31}$P-NMR spectrum, complete degradation of $P_7(SiMe_3)_3$ was observed.

#### 4.5.13.4 Reaction with $HOCN(CH_3)_2$ (DMF)

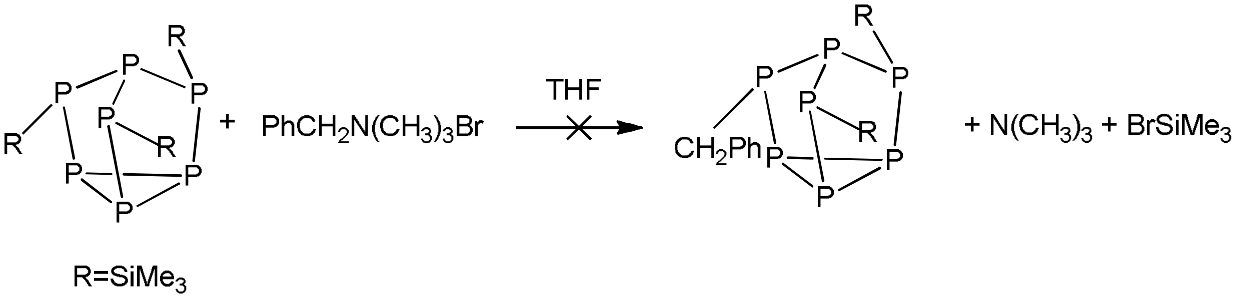


| | | | |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 1.00 g | 436.38 g.mol$^{-1}$ | 2.29 mmol |
| $HOCN(CH_3)_2$ | 0.17 g | 73.10 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL flask, $P_7(SiMe_3)_3$ (1.00 g, 2.29 mmol) was dissolved in dry THF (20 mL) and a solution of dry DMF (0.17 g, 2.29 mmol) was added with a syringe at room temperature under strong stirring. No reaction occurred and the light yellowish solution was stirred for a couple of days (12 days). The $^{31}$P-NMR spectrum of the solution showed no reaction but the typical shifts of $P_7(SiMe_3)_3$.

When $P_7(SiMe_3)_3$ (1.00 g, 1.146 mmol) was dissolved in dry DMF (10mL), the $^{31}$P-NMR spectrum showed the decomposition of the starting material $P_7(SiMe_3)_3$.

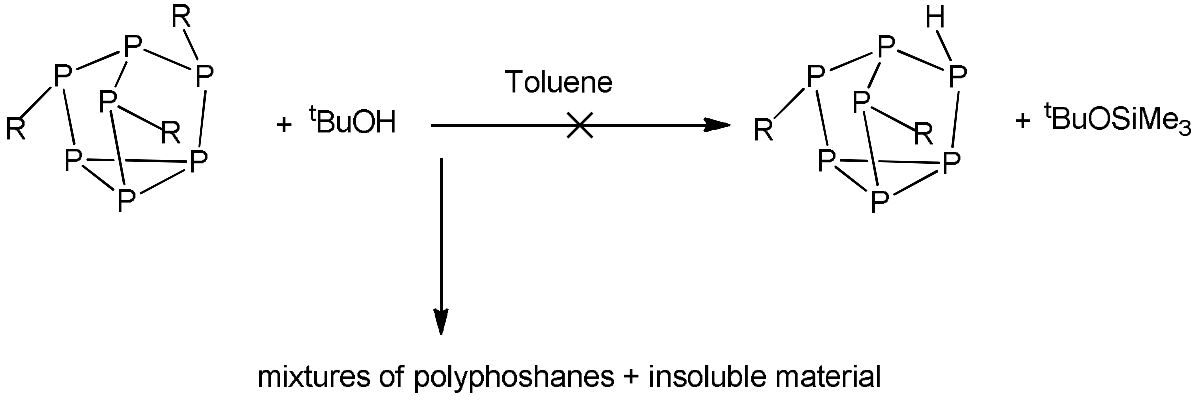
### 4.5.13.5 Reaction with $[PhCH_2NMe_3]^+Br^-$



| | | | |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 0.50 g | 436.38 g.mol$^{-1}$ | 1.15 mmol |
| $PhCH_2N(CH_3)_3Br$ | 0.27 g | 230.12 g.mol$^{-1}$ | 1.15 mmol |

In a 100 mL two necked flask, $P_7(SiMe_3)_3$ (0.50 g, 1.15 mmol) was dissolved in dry THF. $PhCH_2N(CH_3)_3Br$ (0.27 g. 1.15 mmol) was added to the solution at room temperature with a spatula under strong stirring. After a couple of hours, no change in the colour of the solution was observed. A $^{31}$P-NMR analysis showed no reaction. The solution was stirred at room temperature for additional 7 days. According to the $^{31}$P-NMR spectrum, a slow and complete degradation of the starting material $P_7(SiMe_3)_3$ was observed.

### 4.5.13.6 Reaction with ${}^{t}$BuOH

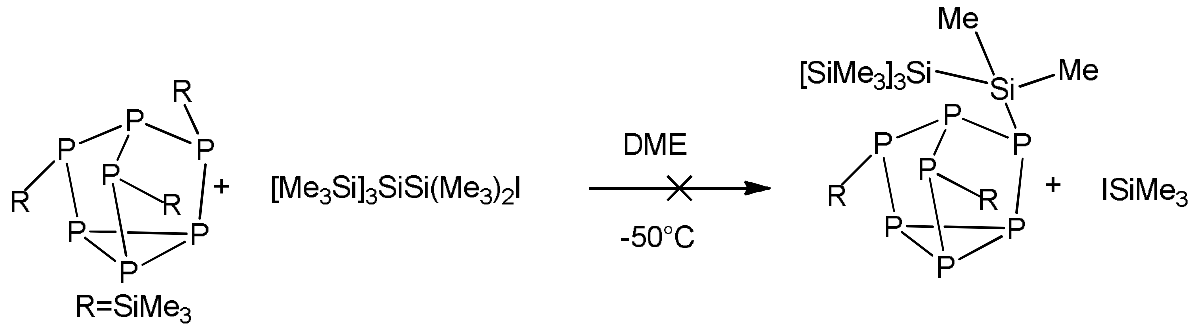


|  |  |  |  |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 1.00 g | 436.38 g.mol$^{-1}$ | 2.29 mmol |
| ${}^{t}$BuOH | 0.17 g | 74.12 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL two necked flask, $P_7(SiMe_3)_3$ (1.00 g, 2.29 mmol) was dissolved in dry toluene (20 mL). A toluene solution of dry ${}^{t}$BuOH (0.17 g, 2.29 mmol) was added with a syringe at room temperature. The yellowish solution was stirred for 8 days and finally showed a dark yellow colour. Light yellowish insoluble material had settled on the bottom of the flask. The ${}^{31}$P-NMR spectrum of the solution showed the presence of a mixture of polyphosphanes. No pure products could be separated by fractional crystallisation.

${}^{31}$P-NMR (toluene): δ = 62.7(m), 7.6 (m), -13.5 (m), -38.0 (m), -51.6 (m), -97.4 (m), -110.3 (m), -132.7 (t), -144.0 (t), -169.8 (m)

### 4.5.13.7 Reaction with $[(Me_3)Si]_3SiSiMe_2I$

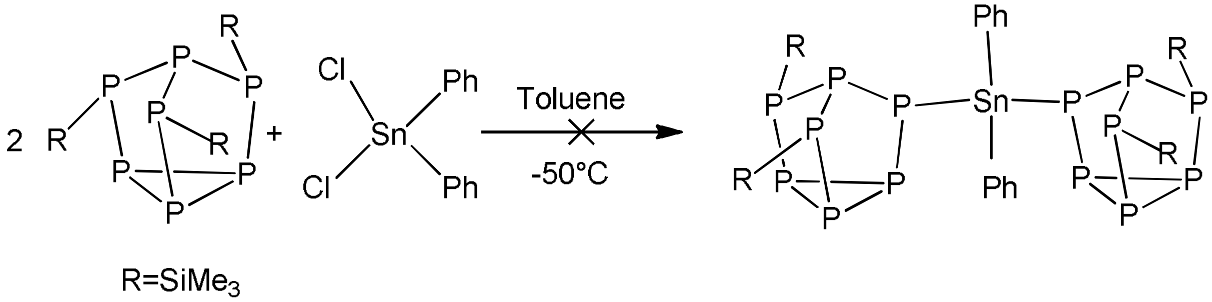


| | | | |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 0.50 g | 436.38 g.mol$^{-1}$ | 1.15 mmol |
| $[(Me_3)Si]_3SiSi(Me_3)_2I$ | 0.49 g | 439.90 g.mol$^{-1}$ | 1.15 mmol |

In a 100 mL two necked flask, $P_7(SiMe_3)_3$ (0.50 g, 1.15 mmol) and $[(Me_3)Si]_3SiSiMe_2I$ (0.49 g, 1.15 mmol) were mixed and cooled down to -50°C. Dry DME (30 mL) was then added dropwise to the mixture under stirring over a period of 20 min. The light yellowish solution was stirred for 18 days and then showed a dark yellowish colour. The advancement of the reaction was checked by $^{31}$P-NMR spectroscopy. A precipitate formed. A $^{31}$P-NMR of the DME solution was performed but showed no signals. The solution was decanted and the precipitate was dissolved in 15 mL of $CS_2$. According to the $^{31}$P-NMR spectrum, a reaction had occurred but the considerable number of signals didn't allow the identification of the products. Crystals could not be obtained. The typical signals of the $P_7$-backbone were present but the target product could not be identified.

$^{31}$P-NMR ($CS_2$): $\delta$ = 104.2 (m), 78.1 (m), 68.2 (m), 29.7 (m), 14.5 (m), -58.1 (m), -100.1 (m), -115.8 (m), -125.8 (m), -145.6 (m), -158.1 (m), -167.3 (m)

#### 4.5.13.8 Reaction with $Cl_2SnPh_2$

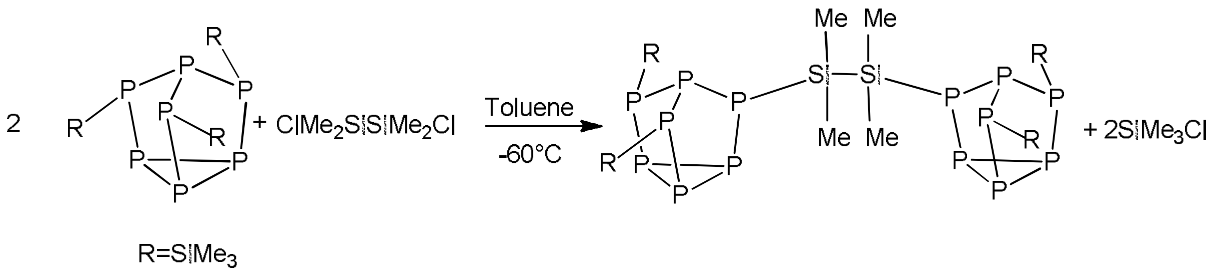


| | | | |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 1.00 g | 436.38 g.mol$^{-1}$ | 2.29 mmol |
| $Cl_2SnPh_2$ | 0.39 g | 343.80 g.mol$^{-1}$ | 1.11 mmol |

In a 100 mL two necked flask, $P_7(SiMe_3)_3$ (1.00 g, 2.29 mmol) and $Cl_2SnPh_2$ (0.39 g, 1.11 mmol) were mixed and cooled to -50°C. A solution of dry DME (40 mL) was added dropwise to the mixture. The reaction mixture was then allowed to warm up to room temperature and a $^{31}$P-NMR spectrum was recorded. No reaction was observed, just the NMR signals of the educt $P_7(SiMe_3)_3$ were present. DME was removed by evaporation and 30 mL toluene was added. The solution was heated to reflux for 1 hour and was allowed to come to room temperature slowly. The solution showed a yellow colour and was stirred for another 2 hours. The product in solution could not be identified with reliability. The presence of seven signals could match with the formation of $(SiMe_3)_2P_7SnPh_2Cl$ or $(SiMe_3)_2P_7P_7(SiMe_3)_2$.

$^{31}$P-NMR (toluene): $\delta$ = 67.55 (m), 38.57 (m), 12.34 (m), -22.25 (m), -101.28 (m), -156.59 (m), -170.78 (m).

### 4.5.13.9 Reaction with $ClSiMe_2SiMe_2Cl$

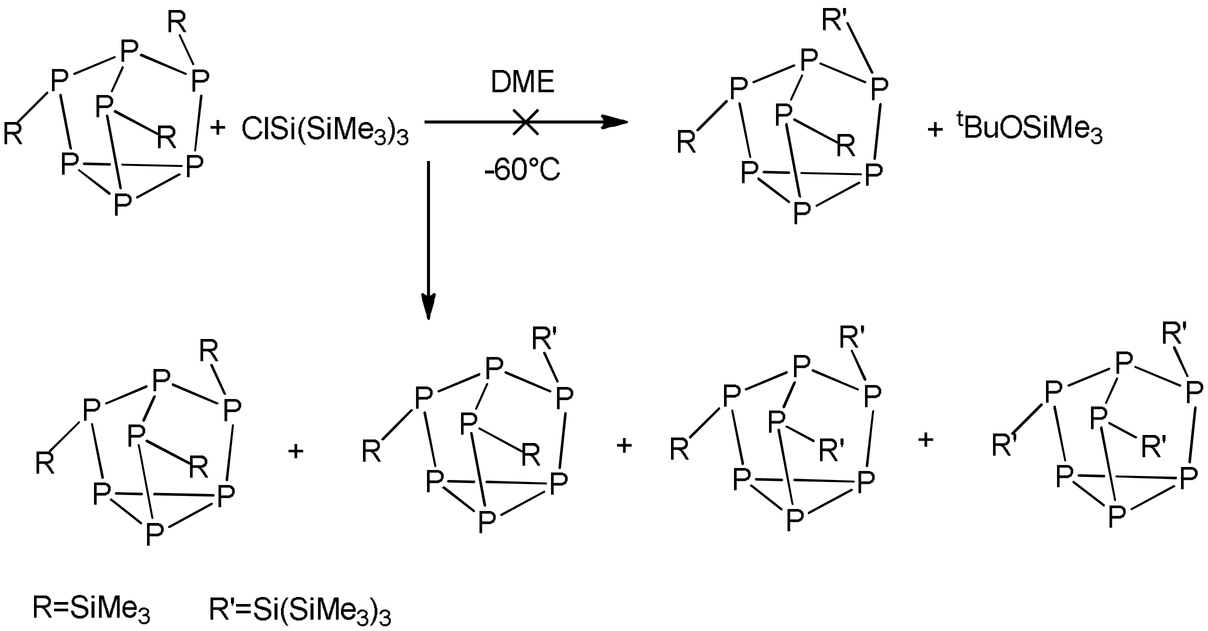


| | | | |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 1.00 g | 436.38 $g.mol^{-1}$ | 2.29 mmol |
| $ClSiMe_2SiMe_2Cl$ | 0.25 g | 283.40 $g.mol^{-1}$ | 1.35 mmol |

In a 100 mL two necked flask, $P_7(SiMe_3)_3$ (1.00 g, 2.29 mmol) and $ClSiMe_2SiMe_2Cl$ (0.25 g, 1.35 mmol) were mixed and cooled to -60°C. A solution of dry toluene (40 mL) was added dropwise to the mixture over a period of 20 minutes under strong stirring. The mixture was stirred at -60 °C for a period of 2h and was then allowed to warm up to room temperature slowly. The solution was kept at room temperature for further 4 days. A $^{31}$P-NMR analysis was performed proving that the desired compound had formed. The product crystallised from n-hexane at -80°C in the form of yellow crystals too small for X-ray analysis

$^{1}$H NMR ($C_6D_6$): δ = 0.27 (d, 36H), 0.12 (d, 12H).
$^{31}$P-NMR ($C_6D_6$): δ = 25.4 (m, 2P), 5.2 (m, 4P), -61.5 (m, 2P), -161.8 (m, 2P), -154.5 (m, 2P), -146.3 (m, 2P).
$^{29}$Si NMR ($C_6D_6$): δ = 2.4 (d, *Si*Me$_3$), $^{1}$J (SiP) ≈ 27 Hz,
δ = -26.5 (d, *Si*Me$_2$), $^{1}$J (SiP) ≈ 47 Hz.
Elemental analysis:
$C_{16}H_{48}Si_6P_{14}$ (842,70): calculated. C 22.8, H 5.74; found C 22.37, H 5.44.

### 4.5.13.10 Reaction of $P_7(SiMe_3)_3$ with one equivalent of $ClSi(SiMe_3)_3$

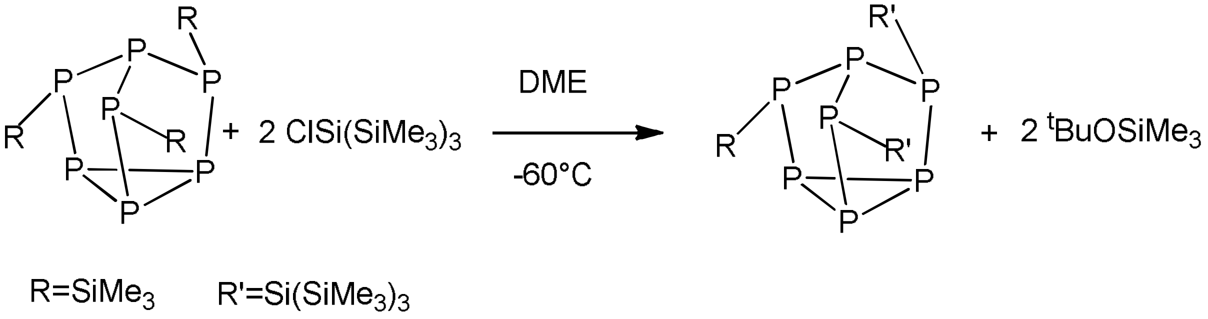


| | | | |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 1.00 g | 436.38 g.mol$^{-1}$ | 2.29 mmol |
| $ClSi(SiMe_3)_3$ | 0.64 g | 283.40 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL two necked flask, $P_7(SiMe_3)_3$ (1.00 g, 2.29 mmol) was dissolved in 40 mL DME. The solution was cooled to -60°C and a solution of $ClSi(SiMe_3)_3$ in 30 mL DME (0.64 g, 2.29 mmol) was added dropwise at that temperature under strong stirring. The solution turned dark yellow immediately. After two hours, the reaction mixture was allowed to warm up to room temperature. DME was removed by evaporation i.v.. The crystalline residue was then dissolved in toluene. A $^{31}$P-NMR analysis showed the presence of a mixture of

$[(SiMe_3)_3Si]P_7(SiMe_3)_2$ and $[(SiMe_3)_3Si]_2P_7(SiMe_3)$ as well as minor quantities of $P_7(SiMe_3)_3$ and$[(SiMe_3)_3Si]_3P_7$.

### 4.5.14 Synthesis of $(SiMe_3)P_7(Si(SiMe_3)_3)_2$



| | | | |
|---|---|---|---|
| $P_7(SiMe_3)_3$ | 1.00 g | 436.3 g.mol$^{-1}$ | 2.29 mmol |
| $ClSi(SiMe_3)_3$ | 1.30 g | 283.4 g.mol$^{-1}$ | 4.58 mmol |

In a 200 ml two necked flask, $P_7(SiMe_3)_3$ (1.00 g, 2.29 mmol) was dissolved in 70 mL DME and the solution was cooled to -60°C. A solution of $ClSi(SiMe_3)_3$ (1.30 g, 4.58 mmol) in 30 mL of DME was added dropwise at that temperature. After two hours, the reaction mixture was allowed to warm up to room temperature, and a precipitate of pure $[(SiMe_3)_3Si]_2PSiMe_3$ formed. DME was removed by evaporation. The crystalline residue was then dissolved in toluene, and colourless crystals of $[(SiMe_3)_3Si]_2PSiMe_3$ precipitated at -80° with a quality suitable for X-ray diffraction. Yield was 1.6 g (≈ 90%).

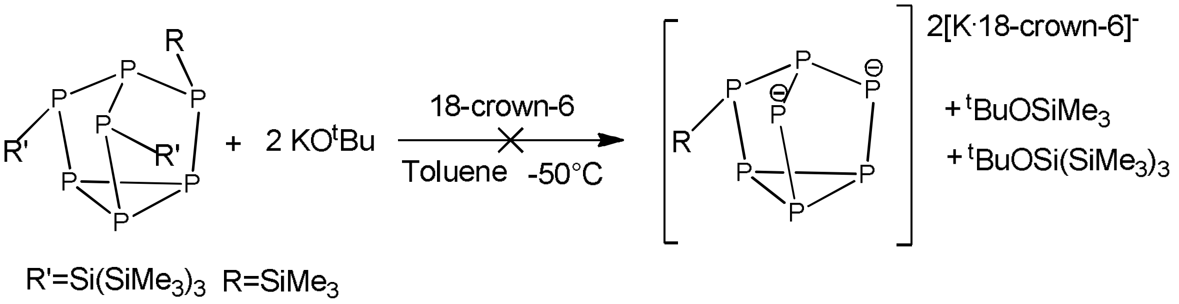
Elemental analysis $C_{21}H_{63}Si_9P_7$ (785.33), calc./found: C: 32.12/31.63%, H: 8.09/7.81%.

$^1H$-NMR ($C_6D_6$): $\delta = 0.37$ (Si(SiMe$_3$), 27H), 0.34 (Si(SiMe$_3$), 27H), 0.22 (SiMe$_3$, d, 9H, $^3J(PH) = 4.8$ Hz).

$^{31}P$-NMR ($C_6D_6$): $\delta = 2.5$ (t, 1P), -4.5 (t, 1P), -11.5 (t, 1P), -101.6 (m, 1P), -148.2 (m, 1P), -166.5 (m, 2P).

$^{29}Si$-NMR ($C_6D_6$): $\delta = 6.6$ (*Si*Me$_3$, d, $^1$JSiP ≈ 37 Hz),
$\delta = -8.8$ (s, Si(*Si*Me$_3$)$_3$),
$\delta = -93.6$ (d, *Si*(SiMe$_3$)$_3$, $^1$JSiP ≈ 93 Hz),
$\delta = -95.3$ (d, *Si*(SiMe$_3$)$_3$, $^1$JSiP ≈ 94 Hz).

### 4.5.14.1 Reaction of $(SiMe_3)P_7(Si(SiMe_3)_3)_2$ with 2 equivalents of $KO^tBu$

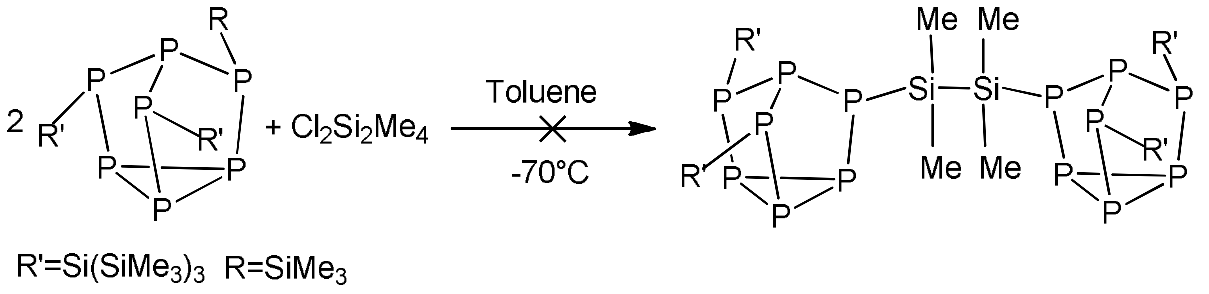


| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 1.00 g | 791.36 g.mol$^{-1}$ | 1.26 mmol |
| $KO^tBu$ | 0.28 g | 112.10 g.mol$^{-1}$ | 2.52 mmol |
| 18-crown-6 | 0.66 g | 264.22 g.mol$^{-1}$ | 2.52 mmol |

In a 100 mL two necked flask, $SiMe_3P_7[Si(SiMe_3)_3]_2$ (1.00 g, 1.26 mmol) was dissolved in dry toluene (15 mL). The solution was cooled to -50°C, and a solution of $KO^tBu$ (0.28 g, 2.52 mmol) and 18-crown-6 (0.66 g, 2.52 mmol) in dry toluene (20 mL) was added dropwise over a period of 10 minutes. The colourless solution slowly turned red and was stirred at -50°C for a period of 1h. The reaction mlixture was then allowed to warm up to room temperature, and insoluble by-products were separated from the solution by decantation. The $^{31}$P-NMR spectrum didn't show the expected shift of the dianion. All attempts to grow crystals failed.

The reaction of $SiMe_3P_7[Si(SiMe_3)_3]_2$ with $KO^tBu$ in a molar ratio 1:1 gives the anion $KP_7[Si(SiMe_3)_3]_2$ (see section 4.5.5)

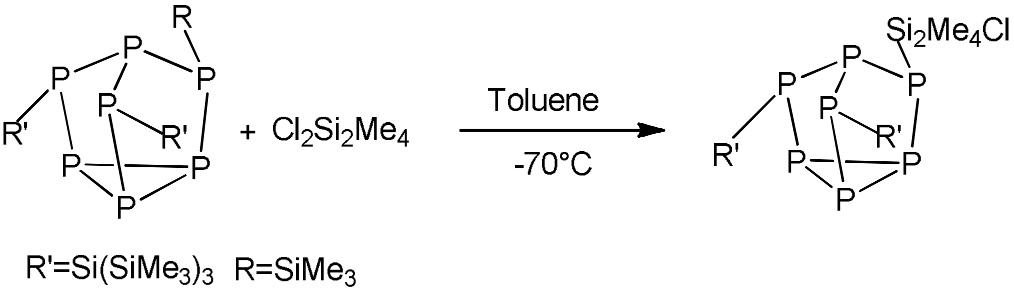
### 4.5.14.2 Reaction of $(SiMe_3)P_7(Si(SiMe_3)_3)_2$ with one equivalent of $Cl_2Si_2Me_4$



| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 1.00 g | 791.36 $g.mol^{-1}$ | 1.26 mmol |
| $ClSiMe_2SiMe_2Cl$ | 0.18 g | 283.40 $g.mol^{-1}$ | 0.63 mmol |

In a 100 mL two necked flask, $ClSiMe_2SiMe_2Cl$ (0.18 g, 0.63 mmol) and $SiMe_3P_7[Si(SiMe_3)_3]_2$ (1.00 g, 1.26 mmol) were mixed. The mixture was cooled to -70°C and a solution of dry toluene (50 mL) was added dropwise over a period of 20 minutes under strong stirring. The solution was stirred at -70 °C for a period of 2 hours. The mixture was then allowed to come to room temperature very slowly and was stirred at room temperature for 4 days. According to the $^{31}P$-NMR spectrum, the solution contained the starting material $SiMe_3P_7[Si(SiMe_3)_3]_2$ and obviously $[Si(SiMe_3)_3]_2P_7Si_2Me_4Cl$.

### 4.5.14.3 Reaction of $(SiMe_3)P_7(Si(SiMe_3)_3)_2$ with 2 equivalents of $Cl_2Si_2Me_4$

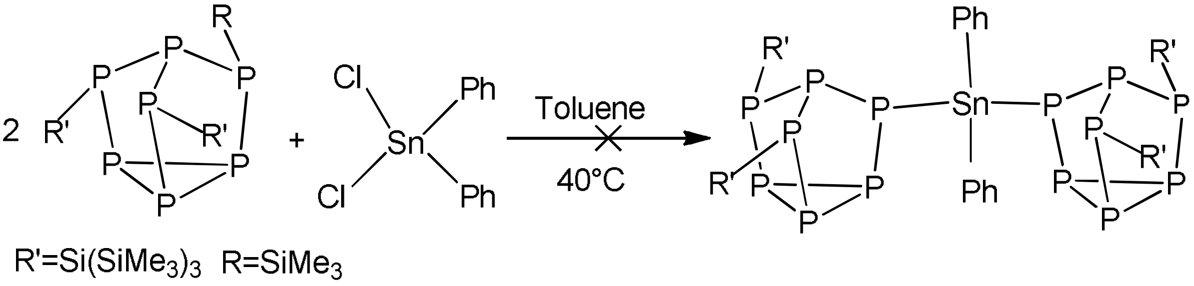


| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 1.00 g | 791.36 g.mol$^{-1}$ | 1.26 mmol |
| $ClSiMe_2SiMe_2Cl$ | 0.36 g | 283.40 g.mol$^{-1}$ | 1.26 mmol |

In a 100 mL two necked flask, $ClSiMe_2SiMe_2Cl$ (0.36 g, 1.26 mmol) and $SiMe_3P_7[Si(SiMe_3)_3]_2$ (1.00 g, 1.26 mmol) were mixed together. The mixture was cooled to -70°C and a solution of dry toluene (50 mL) was added dropwise over a period of 20 minutes under strong stirring. The solution was stirred at -70 °C for a period of 2h. The mixture was very slowly warmed up to room temperature, and was kept at room temperature for 4 days. According to the $^{31}$P-NMR spectrum, the solution contained $[Si(SiMe_3)_3]_2P_7Si_2Me_4Cl$.

$^{31}$P-NMR (THF), δ: 4.4 (t, 1P), -8.2 (m, 2P), -100.7 (q, 1P), -153.0 (m, 1P), -166.4 (m, 2P).

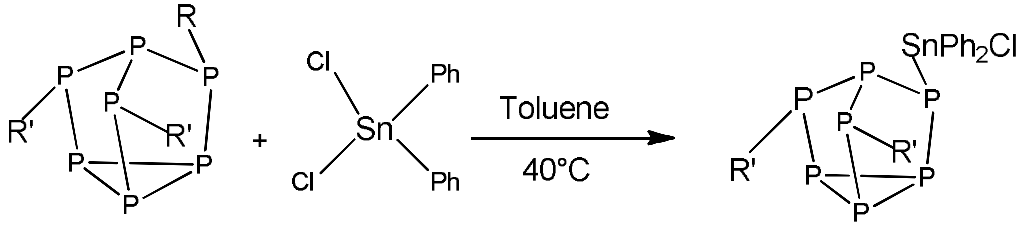
### 4.5.14.4 Reaction of $(SiMe_3)P_7(Si(SiMe_3)_3)_2$ with one equivalent of $Cl_2SnPh_2$



| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 1.00 g | 791.36 $g.mol^{-1}$ | 1.26 mmol |
| $Cl_2SnPh_2$ | 0.22 g | 343.80 $g.mol^{-1}$ | 0.63 mmol |

In a 100 mL two necked flask, $SiMe_3P_7[Si(SiMe_3)_3]_2$ (1.00 g, 1.26 mmol) and $Cl_2SnPh_2$ (0.22 g, 0.63 mmol) were mixed together and cooled to -50°C. A solution of dry toluene (60 mL) was added dropwise to the mixture over a period of 30 min. The mixture was stirred at -50°C for a period of 1 hour and was then allowed to come to room temperature. No reaction could be observed, just the signals of $SiMe_3P_7[Si(SiMe_3)_3]_2$ could be observed. The solution was heated to 40°C for one month. According to the $^{31}P$-NMR spectrum, the solution contained the starting material $SiMe_3P_7[Si(SiMe_3)_3]_2$ and $[Si(SiMe_3)_3]_2P_7SnPh_2Cl$ (see 4.5.14.5. for NMR data of $[Si(SiMe_3)_3]_2P_7SnPh_2Cl$)

### 4.5.14.5 Reaction of $(SiMe_3)P_7(Si(SiMe_3)_3)_2$ with 2 equivalents of $Cl_2SnPh_2$



R'=Si(SiMe3)3 R=SiMe3

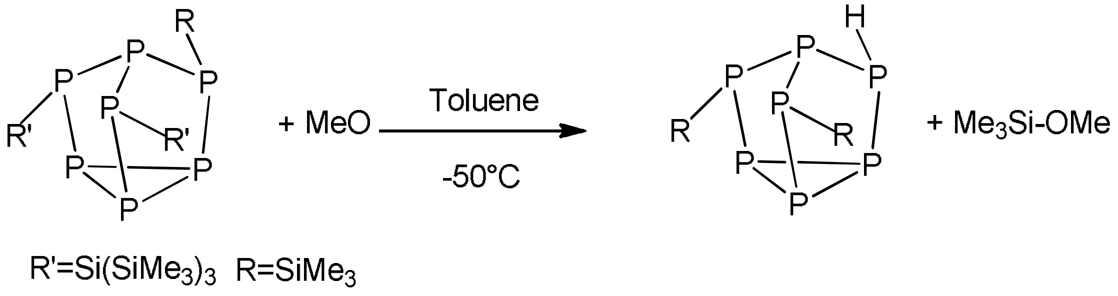
| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 1.00 g | 793.0 g.mol$^{-1}$ | 1.26 mmol |
| $Cl_2SnPh_2$ | 0.44 g | 342.7 g.mol$^{-1}$ | 1.26 mmol |

In a 100 mL two necked flask, $SiMe_3P_7[Si(SiMe_3)_3]_2$ (1.00 g, 1.26 mmol) and $Cl_2SnPh_2$ (0.44 g, 1.26 mmol) were mixed together. A solution of dry toluene (60 mL) was added dropwise to the mixture at room temperature. The solution was heated to 40°C for 7 days. According to the $^{31}$P-NMR spectrum, the solution contained $[Si(SiMe_3)_3]_2P_7SnPh_2Cl$.

$^{31}$P-NMR (THF), δ: 17. (t, 1P), 9.7 (tt, 2P), -99.5 (q, 1P), -155.4 (m, 2P), -166.4 (m, 1P).

$^{29}$Si NMR (THF): δ: 8.8 (s, Si(*Si*Me$_3$)$_3$)
δ: -88.6 (d, *Si*(SiMe$_3$)$_3$), $^1$J (SiP) ≈ 94 Hz)
δ: -91.4 (d, *Si*(SiMe$_3$)$_3$), $^1$J (SiP) ≈ 94 Hz)

### 4.5.14.6 Reaction of $(SiMe_3)P_7(Si(SiMe_3)_3)_2$ with ROH with R= Me, $^t$Bu



| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 1.00 g | 793.0 g.mol$^{-1}$ | 1.26 mmol |
| MeOH | 0.04 g | 31.0 g.mol$^{-1}$ | 1.26 mmol |

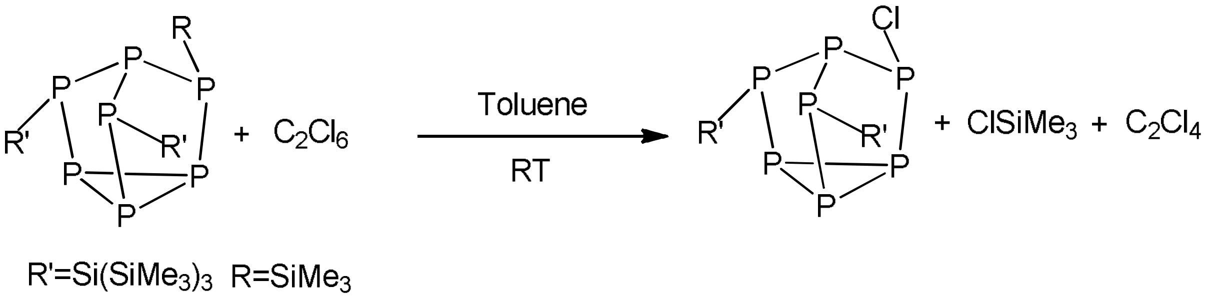
In a 100 mL two necked flask, $SiMe_3P_7[Si(SiMe_3)_3]_2$ (1.00 g, 1.26 mmol) was dissolved in dry toluene. A solution of MeOH in dry toluene (0.04 g, 1.26 mmol) was added dropwise at -60°C. The solution turned yellow and was stirred at -50°C for 2 hours. It was then allowed to warm to room temperature. According to the $^{31}$P-NMR spectrum, the solution contained $HP_7[Si(SiMe_3)]_2$.

The same result was obtained using $^t$BuOH.

$^{31}$P-NMR ($C_6D_6$), δ: 15.7 (t, 1P), -7.7 (m, 2P), -109.6 (m, 1P), -156.2 (m, 2P), -173.1 (m, 1P).

(see section 4.5.12.4 for complete analysis of $HP_7[Si(SiMe_3)]_2$)

### 4.5.15 Synthesis of $ClP_7[Si(SiMe_3)_3]_2$



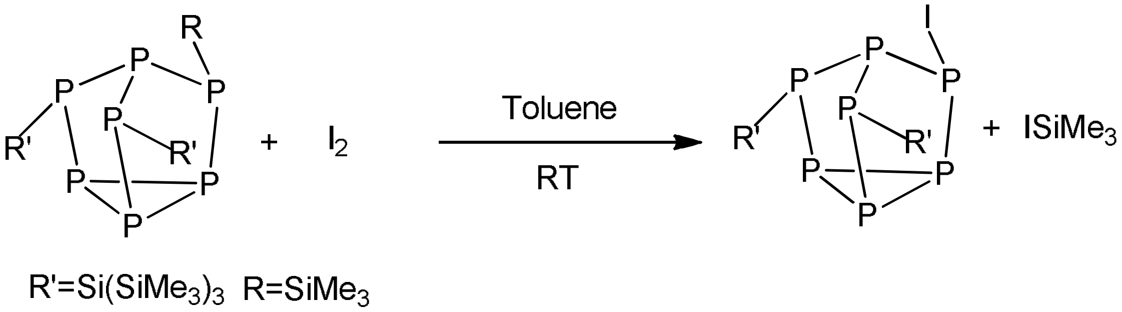
| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 0.50 g | 785.02 g.mol$^{-1}$ | 0.64 mmol |
| $C_2Cl_6$ | 0.15 g | 236.74 g.mol$^{-1}$ | 0.64 mmol |

In a 100 mL two necked flask, $SiMe_3P_7[Si(SiMe_3)_3]_2$ (0.50 g, 0.637 mmol) was dissolved in dry toluene (20 mL). $C_2Cl_6$ (0.15 g, 0.637 mmol) was added with a spatula to the solution under strong stirring. The mixture was stirred for 7 days at 40°C. The colour of the solution slowly changed to light orange. The advancement of the reaction was checked by $^{31}$P-NMR. Insoluble by-products had formed. The solution was separated from the insoluble material by decantation. The solvent, $C_2Cl_4$ and $SiMe_3Cl$ were removed by evaporation i.v.. Traces of $Si(SiMe_3)_3Cl$ formed by slow decomposition of $ClP_7[Si(SiMe_3)_3]_2$ were eliminated by sublimation at 60°C. Despite many attempts, crystals could not be obtained.

$^{31}$P-NMR (Toluene), δ: 175.4 (m, 1P), -4.8 (m, 1P), -56.6 (m, 1P), -97.3 (m, 1P), -153.2 (m, 2P), -192.3 (m, 1P).

$^{29}$Si NMR (Toluene): δ = 8.6 (s, *Si*Me$_3$),
δ = -92.1 (d, *Si*(SiMe$_3$)$_3$, $^1$JSiP ≈ 104 Hz),
δ = -94.5 (d, *Si*(SiMe$_3$)$_3$, $^1$JSiP ≈ 94 Hz).

### 4.5.16 Synthesis of $IP_7[Si(SiMe_3)_3]_2$



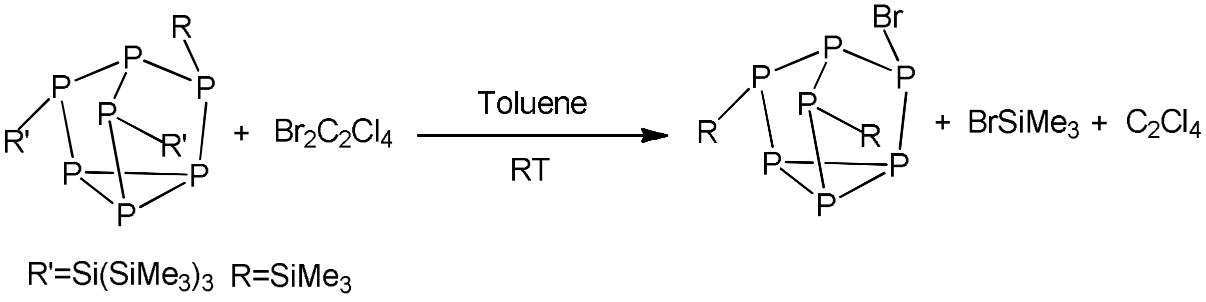
| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 1.00 g | 785.02 g.mol$^{-1}$ | 1.27 mmol |
| $I_2$ | 0.23 g | 253.81 g.mol$^{-1}$ | 1.27 mmol |

In a 100 mL two necked flask, $SiMe_3P_7[Si(SiMe_3)_3]_2$ (1.00 g, 1.27 mmol) was dissolved in dry toluene (25 mL). $I_2$ (0.23 g, 1.27 mmol) was added to the solution with a spatula under strong stirring. The colour of the solution changed to light orange. The mixture was stirred for 8 days at room temperature and the advancement of the reaction was checked by NMR. Insoluble by-products had formed. The solution was separated from the insoluble material by decantation. The solvent and $SiMe_3I$ were then removed by evaporation i.v.. $Si(SiMe_3)_3I$ formed by the slow decomposition of $IP_7[Si(SiMe_3)_3]_2$ was removed by sublimation at 40°C. All attempts to obtain crystals were unsuccessful.

$^{31}$P-NMR (Toluene), δ: 85.6 (m, 1P), -5.8 (m, 1P), -40.2 (m, 1P), -98.6 (m, 1P), -155.2 (m, 2P), -179.3 (m, 1P).

$^{29}$Si NMR (Toluene): δ = 8.8 (s, *Si*Me$_3$),
δ = -91.9 (d, *Si*(SiMe$_3$)$_3$, $^1$JSiP ≈ 137 Hz),
δ = -94.2 (d, *Si*(SiMe$_3$)$_3$, $^1$JSiP ≈ 96 Hz).

### 4.5.17 Synthesis of $BrP_7[Si(SiMe_3)_3]_2$



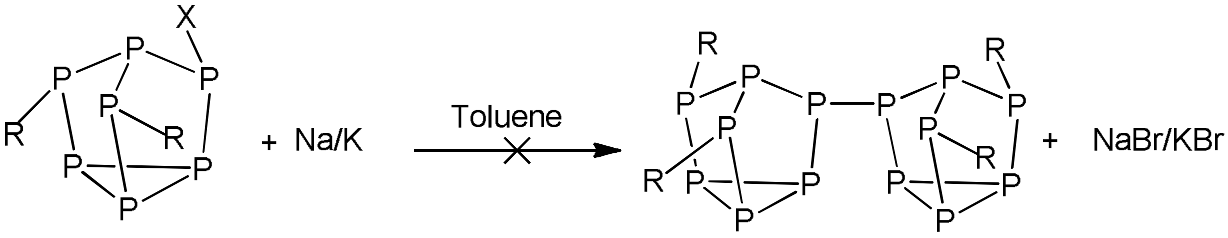
| | | | |
|---|---|---|---|
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 0.50 g | 785.02 g.mol$^{-1}$ | 0.64 mmol |
| $Br_2C_2Cl_4$ | 0.21 g | 324.30 g.mol$^{-1}$ | 0.64 mmol |

In a 100 mL two necked flask $SiMe_3P_7[Si(SiMe_3)_3]_2$ (0.50 g, 0.64 mmol) was dissolved in dry toluene (20 mL). $Br_2C_2Cl_4$ (0.21 g, 0.64 mmol) was added to the solution with a spatula under strong stirring. The colour of the solution did not change. The mixture was stirred for 7 days at 40°C and the advancement of the reaction was checked by $^{31}$P-NMR. Insoluble by-products had formed. The solution was separated from the insoluble material by decantation. The solvent, $C_2Cl_4$ and $SiMe_3Br$ were then removed by evaporation i.v.. $Si(SiMe_3)_3Br$ formed by the slow decomposition of $BrP_7[Si(SiMe_3)_3]_2$ was then removed by sublimation at 60°C. Crystals could not be obtained.

$^{31}$P-NMR (Toluene), δ: 145.2 (m, 1P), -1.5 (m, 1P), -53.2 (m, 1P), -97.9 (m, 1P), -152.1 (m, 2P), -188.4 (m, 1P).

$^{29}$Si NMR (Toluene): δ = 8.7 (s, *Si*Me$_3$),
δ = -92.2 (d, *Si*(SiMe$_3$)$_3$, $^1$JSiP ≈ 98 Hz),
δ = -94.5 (d, *Si*(SiMe$_3$)$_3$, $^1$JSiP ≈ 94 Hz).

### 4.5.18 Reaction of $BrP_7[Si(SiMe_3)_3]_2$ with Na/K

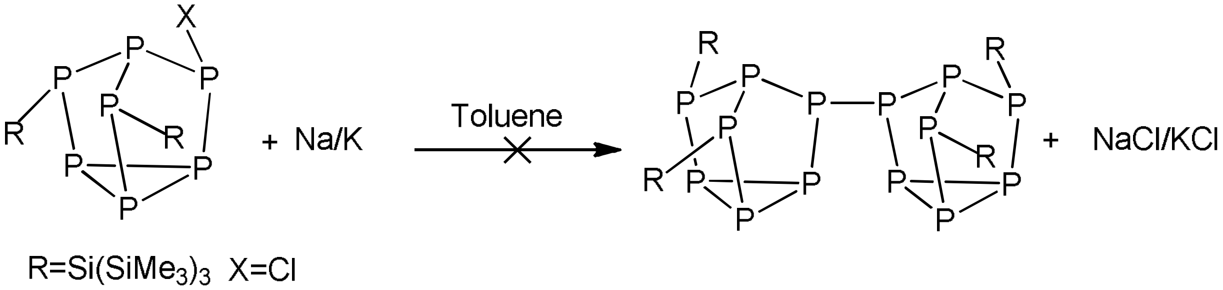


R=$Si(SiMe_3)_3$ X=Br

| | | | |
|---|---|---|---|
| $BrP_7[Si(SiMe_3)_3]_2$ | | | 0.64 mmol |
| Na/K | 0.10 g | 62.08 $g.mol^{-1}$ | 1.61 mmol |

In a 100 mL two necked flask $BrP_7[Si(SiMe_3)_3]_2$ (0.67 mmol prepared from 0.50 g of $SiMe_3P_7[Si(SiMe_3)_3]_2$ and 0.42 g of $Br_2C_2Cl_4$) was first synthesized in toluene at room temperature. The solvent and $SiMe_3Br$ was then removed by evaporation i.v.. $BrP_7[Si(SiMe_3)_3]_2$ was dissolved in toluene and excess of Na/K alloy (0.10 g, 1.61 mmol) was added with a syringe at room temperature under strong stirring. The colour of the solution did not change. The mixture was stirred for 4 hours at room temperature, and the advancement of the reaction was checked by $^{31}$P-NMR. The solution was finally separated from the salts by decantation. The $^{31}$P-NMR spectrum showed just the typical shifts of $P_7[Si(SiMe_3)_3]_3$.

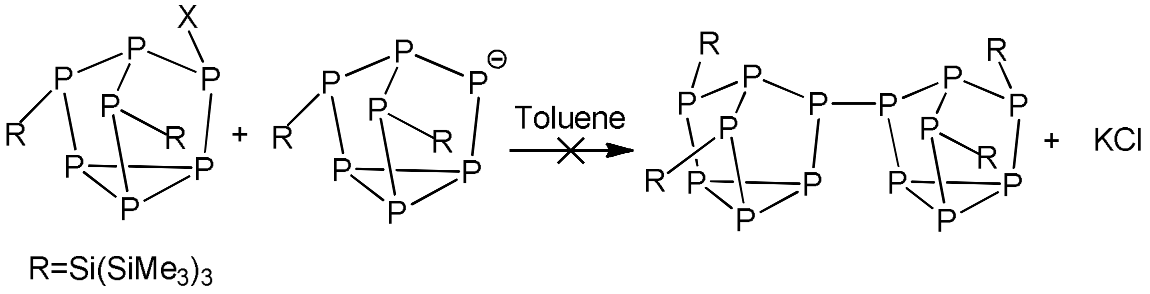
### 4.5.19 Reaction of $ClP_7[Si(SiMe_3)_3]_2$ with Na/K



| | | | |
|---|---|---|---|
| $ClP_7[Si(SiMe_3)_3]_2$ | | | 0.67 mmol |
| Na/K | 0.10 g | 62.08 $g.mol^{-1}$ | 1.61 mmol |

In a 100 mL two necked flask, $ClP_7[Si(SiMe_3)_3]_2$ (0.67 mmol prepared from 0.50 g of $SiMe_3P_7[Si(SiMe_3)_3]_2$ and 0.15 g of $C_2Cl_6$) was first synthesized in toluene. The solvent, $C_2Cl_4$ and $SiMe_3Cl$ were removed by evaporation in vacuum, and $Si(SiMe_3)_3Cl$ was removed by sublimation at 40°C. $ClP_7[Si(SiMe_3)_3]_2$ was dissolved in toluene and Na/K alloy (0.10 g, 1.61 mmol) was added with a syringe at room temperature under strong stirring. The colour of the solution changed to light yellow. The mixture was stirred for 2 hours at room temperature, and the advancement of the reaction was checked by $^{31}$P-NMR. The solution was finally separated from the salts by decantation. The $^{31}$P-NMR spectrum showed the typical shift of $P_7[Si(SiMe_3)_3]_3$.

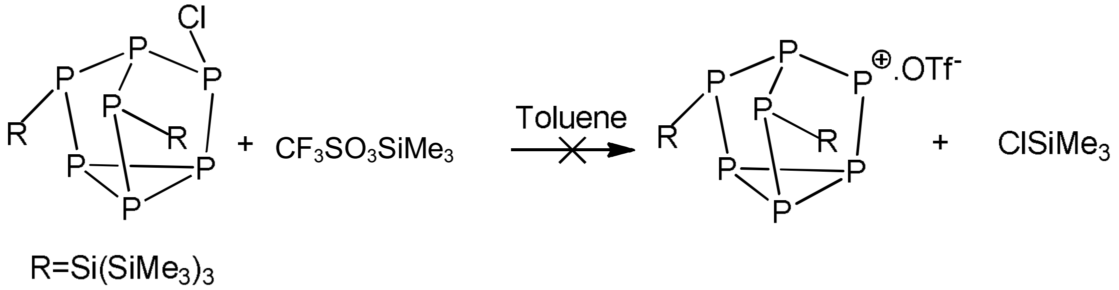
### 4.5.20 Reaction of $ClP_7[Si(SiMe_3)]_2$ with $K^+[P_7(Si(SiMe_3)_3)_2]^-$



| | | | |
|---|---|---|---|
| $ClP_7[Si(SiMe_3)_3]_2$ | | | 1.34 mmol |
| $SiMe_3P_7[Si(SiMe_3)_3]_2$ | 1.00 g | 791.36 $g.mol^{-1}$ | 1.26 mmol |
| $KO^tBu$ | 0.14 g | 112.21 $g.mol^{-1}$ | 1.26 mmol |
| 18-crown-6 | 0.33 g | 264.22 $g.mol^{-1}$ | 1.26 mmol |

In a 100 mL two necked flask, $ClP_7[Si(SiMe_3)_3]_2$ (1.34 mmol prepared from 1.00 g of $SiMe_3P_7[Si(SiMe_3)_3]_2$ and 0.30 g of $C_2Cl_6$) was first synthesized in toluene. The solvent, $C_2Cl_4$ and $SiMe_3Cl$ were removed by evaporation in vacuum, and $Si(SiMe_3)_3Cl$ was removed by sublimation at 40°C. $K^+P_7[Si(SiMe_3)_3]_2^-$ was synthesized (1.27 mmol prepared from 1.00 g of $SiMe_3P_7[Si(SiMe_3)_3]_2$, 0.14 g of $KO^tBu$ and 0.33 g of 18-crown-6) in 20 mL toluene. $ClP_7[Si(SiMe_3)]_2$ was dissolved in toluene and $K^+P_7[Si(SiMe_3)]_2^-$ was added dropwise at -50°C over a period of 20 min. The mixture was stirred at -30°C for 2 hours. The temperature was then allowed to rise to room temperature. The colour of the solution had changed to light yellow. The solution was finally separated from the salts by decantation. The $^{31}P$-NMR spectrum showed just the typical signals of $P_7[Si(SiMe_3)_3]_3$.

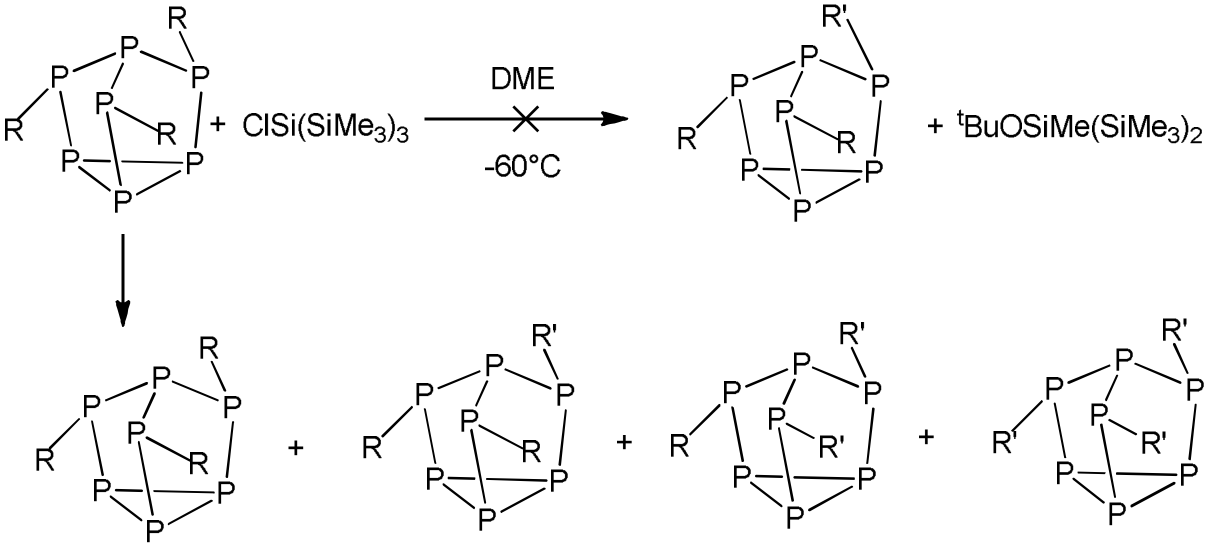
### 4.5.21 Reaction of $ClP_7(Si(SiMe_3)_3)_2$ with $CF_3SO_3SiMe_3$



| | | | |
|---|---|---|---|
| $ClP_7[Si(SiMe_3)]_2$ | | | 0.67 mmol |
| $CF_3SO_3SiMe_3$ | 0.15 g | 222.26 g.mol$^{-1}$ | 0.67 mmol |

In a 100 mL two necked flask, $ClP_7[Si(SiMe_3)_3]_2$ (1.34 mmol prepared from 1.00 g of $SiMe_3P_7[Si(SiMe_3)_3]_2$ and 0.30 g of $C_2Cl_6$) was first synthesized in toluene at room temperature. The solvent and $SiMe_3Cl$ were then removed in vacuum. $ClP_7[Si(SiMe_3)_3]_2$ was dissolved in toluene and cooled to -50°C. A toluene solution (5 mL) of trimethylsilyl trifluoromethylsulfonate $CF_3SO_3SiMe_3$ (0.15 g, 0.67 mmol) was added dropwise over a period of 5 min. The mixture was stirred at low temperature for a period of 1 hour, and slowly warmed up to room temperature. A $^{31}$P-NMR of the light yellowish solution was recorded. The spectrum showed the complete decomposition of the $P_7$-backbone.

### 4.5.22 Reaction of $P_7[SiMe(SiMe_3)_2]_3$ with one equivalent of $ClSi(SiMe_3)_3$

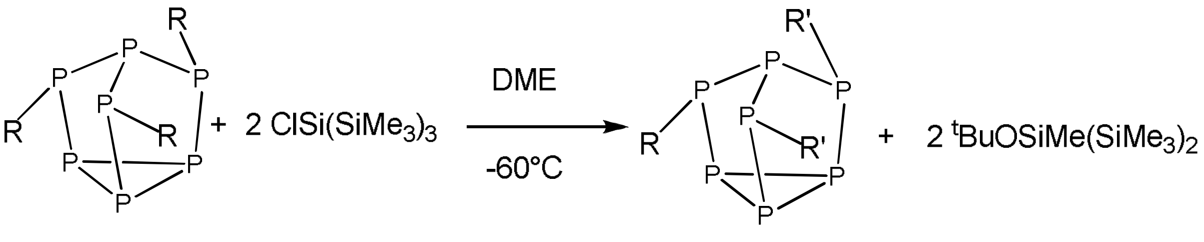


$R=SiMe_3$  $R'=SiMe(SiMe_3)_2$

| | | | |
|---|---|---|---|
| $P_7[SiMe(SiMe_3)_2]_3$ | 0.50 g | 785.40 g.mol$^{-1}$ | 0.64 mmol |
| $ClSi(SiMe_3)_3$ | 0.16 g | 283.4 g.mol$^{-1}$ | 0.64 mmol |

In a 100 mL two necked flask, $P_7[SiMe(SiMe_3)_2]_3$ (0.50 g, 0.64 mmol) was dissolved in 40 mL of DME. The solution was cooled to -50°C and a solution of $ClSi(SiMe_3)_3$ in 10 mL of DME (0.16 g, 0.64 mmol) was added dropwise at that temperature under strong stirring. The colour changed to dark yellow. After two hours, the reaction mixture was allowed to warm to room temperature, and DME was removed by evaporation in vacuum. The crystalline residue was then dissolved in toluene. A $^{31}$P-NMR analysis showed the presence of a mixture of $[(SiMe_3)_3Si]P_7SiMe(SiMe_3)_2$ and $[(SiMe_3)_3Si]_2P_7(SiMe(SiMe_3)$, as well as minor quantities of $[(SiMe_3)_3Si]_3P_7$ and $P_7[SiMe(SiMe_3)_2]_3$.

### 4.5.23 Synthesis of $[Si(SiMe_3)_3]_2P_7(SiMe(SiMe_3)_2)$



R=SiMe(SiMe$_3$)$_2$ R'=Si(SiMe$_3$)$_3$

| | | | |
|---|---|---|---|
| $P_7(SiMe(SiMe_3)_2)_3$ | 1.00 g | 785.40 g.mol$^{-1}$ | 2.29 mmol |
| $ClSi(SiMe_3)_3$ | 1.30 g | 283.40 g.mol$^{-1}$ | 4.58 mmol |

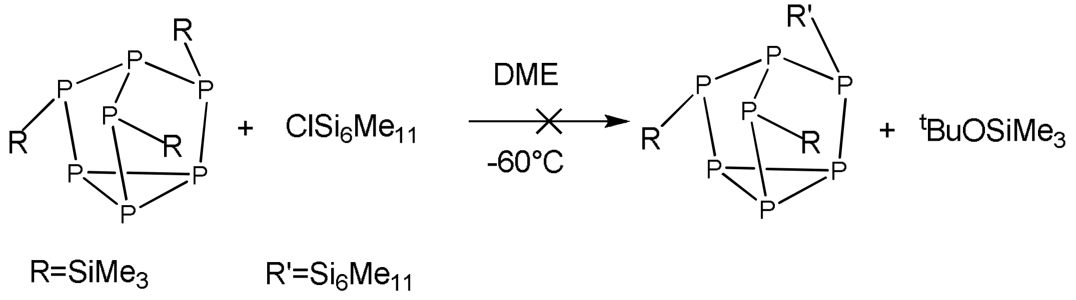
A solution of $P_7[SiMe(SiMe_3)_2]_3$ (1.00 g, 2.29 mmol) in 70 mL of DME was cooled to -60°C, and a solution of $ClSi(SiMe_3)_3$ (1.30 g, 4.58 mmol) in DME (30 mL) was added dropwise at -60°C. A precipitate of pure $[(SiMe_3)_3Si]_2P_7SiMe(SiMe_3)_2$ formed. After two hours, the reaction mixture was allowed to come to room temperature, and DME was removed by evaporation in vacuum. The crystalline residue was then dissolved in toluene, and colourless crystals of $[(SiMe_3)_3Si]_2P_7SiMe(SiMe_3)_2$ precipitated at -80°C with a quality suitable for X-ray diffraction. Yield was 1.6 g (≈ 90%).

$^1$H-NMR ($C_6D_6$): $\delta$ = 0.4 ($Si(SiMe_3)$, 27H), $\delta$ = 0.4 ($Si(SiMe_3)$, 27H), $\delta$ = 0.2 ($SiMe_3$, d, 9H, $^3J(PH)$ = 4.8 Hz).

$^{31}$P-NMR ($C_6D_6$): $\delta$ = 4.1 ppm (1P), $\delta$ = -8.3 ppm (2P), $\delta$ = -96 ppm (1P), $\delta$ = -165 ppm (3P)

$^{29}$Si-NMR: $\delta$ = -11.5 ppm ($\mathit{Si}Me_3$), $\delta$ = -51.7 ppm ($\mathit{Si}Me$), $^1J(SiP)$ = 83.5 ± 5 Hz.
$\delta$ = -8.8 (s, $Si(\mathit{Si}Me_3)_3$),
$\delta$ = -93.3 (d, $\mathit{Si}(SiMe_3)_3$, $^1JSiP$ ≈ 93 Hz),
$\delta$ = -95.3 (d, $\mathit{Si}(SiMe_3)_3$, $^1JSiP$ ≈ 94 Hz).

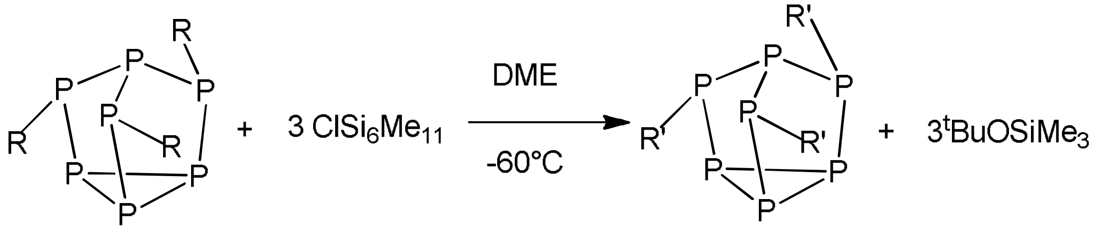
### 4.5.24 Reaction of $P_7(SiMe_3)_3$ with one equivalent of $ClSi_6Me_{11}$



| | | | |
|---|---|---|---|
| $P_7SiMe_3$ | 1.00 g | 436.38 g.mol$^{-1}$ | 2.29 mmol |
| $ClSi_6Me_{11}$ | 0.82 g | 360.50 g.mol$^{-1}$ | 2.29 mmol |

In a 100 mL two necked flask, $P_7(SiMe_3)_3$ (1.00 g, 2.29 mmol) and $ClSi_6Me_{11}$ (0.82 g, 2.29 mmol) were mixed and cooled to -50°C. Dry DME (70mL) was added dropwise at that temperature under strong stirring. The light yellowish solution was then allowed to warm up to room temperature. The solution was stirred for 3 days. A $^{31}P$-NMR analysis showed the presence of a mixture of $P_7(SiMe_3)_3$, $(Si_6Me_{11})P_7(SiMe_3)_2$, $(Si_6Me_{11})_2P_7(SiMe_3)$ and $P_7(Si_6Me_{11})_3$.

### 4.5.25 Reaction of $P_7(SiMe_3)_3$ with three equivalents of $ClSi_6Me_{11}$



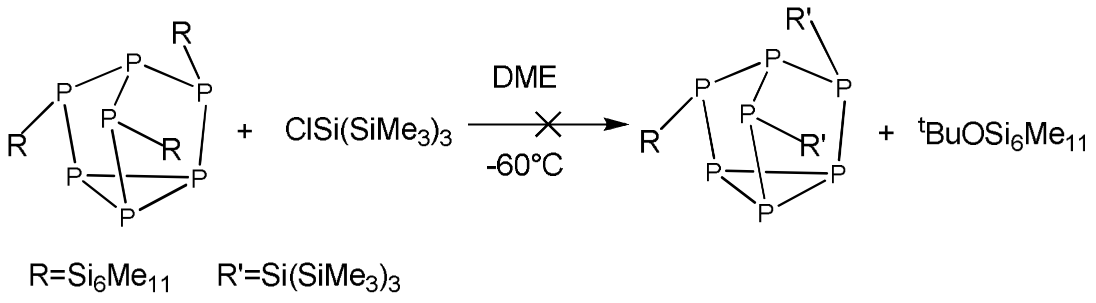
R=$SiMe_3$ R'=$Si_6Me_{11}$

| | | | |
|---|---|---|---|
| $P_7SiMe_3$ | 1.00 g | 436.38 g.mol$^{-1}$ | 2.29 mmol |
| $ClSi_6Me_{11}$ | 2.47 g | 360.50 g.mol$^{-1}$ | 6.87 mmol |

In a 100 mL two necked flask, $P_7(SiMe_3)_3$ (1.00 g, 2.29 mmol) and $ClSi_6Me_{11}$ (2.47 g, 6.87 mmol) were mixed and cooled to -50°C. Dry DME (70mL) was added dropwise at that temperature under strong stirring. The light yellowish solution was then allowed to come to room temperature, and was stirred for 3 days. A $^{31}$P-NMR analysis was performed. The presence of pure $P_7(Si_6Me_{11})_3$ could be observed.

$^{31}$P-NMR (DME): $\delta$ = -0.4 ppm (3P), $\delta$ = -83.1 ppm (1P), $\delta$ = -169.9 ppm (3P)

### 4.5.26 Reaction of $P_7(Si_6Me_{11})_3$ with one equivalent of $ClSi(SiMe_3)_3$



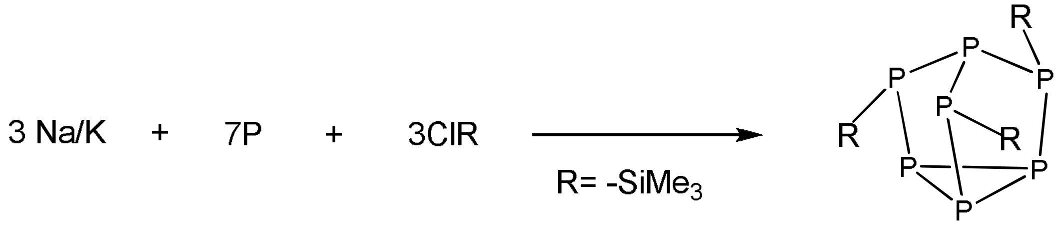
| | | | |
|---|---|---|---|
| $P_7(Si_6Me_{11})_3$ | 1.00 g | 1218.50 g.mol$^{-1}$ | 0.803 mmol |
| $ClSi(Si_3Me_3)_3$ | 0.23 g | 283.4 g.mol$^{-1}$ | 0.803 mmol |

In a 100 mL two necked flask $P_7(Si_6Me_{11})_3$ (1.0 g, 0.803 mmol) and $ClSi(SiMe_3)_3$ (0.23 g, 0.803 mmol) were mixed and cooled to -50°C. Dry toluene (50mL) was added dropwise at that temperature under strong stirring. The yellowish solution was then allowed to come to room temperature. After 4 days stirring a $^{31}$P-NMR analysis showed no reaction. The solution was heated to reflux for 5 days but no reaction occurred. The $^{31}$P-NMR displayed the signals of $P_7(Si_6Me_{11})_3$, The $^{29}$Si-NMR showed the unreacted $ClSi(SiMe_3)_3$.

$^{31}$P-NMR ($C_6D_6$): δ = -0.4 ppm (3P), δ = -83.1 ppm (1P), δ = -169.9 ppm (3P)

## 4.6 Synthesis of reactants

### 4.6.1 Synthesis of $P_7(SiMe_3)_3$



| | | | |
|---|---|---|---|
| K | 7.00 g | 39.10 $g.mol^{-1}$ | 179.04 mmol |
| Na | 5.30 g | 22.99 $g.mol^{-1}$ | 230.54 mmol |
| P | 29.60 g | 30.97 $g.mol^{-1}$ | 955.64 mmol |
| $Me_3SiCl$ | 45.00 g | 108.62 $g.mol^{-1}$ | 414.28 mmol |

In a dry 1 L round bottom three-necked flask a liquid alloy was formed from sodium (5.30 g, 230.54 mmol) and potassium (7.00 g, 179.04 mmol) by gently heating. After cooling, this alloy was covered by dry DME and the solvent was heated to reflux temperature. Red phosphorus (29.60 g, 955.64 mmol) was added and the mixture was again heated to reflux for 48h. DME was then removed from the yellowish-green suspension by evaporation i.v. at ambient temperature. The heptaphosphanide $M_3P_7$ was suspended in about 500 mL of toluene. Then a solution of $ClSiMe_3$ (414.28 mmol, 45.00 g) in 200 mL of toluene was added dropwise at room temperature over a period of 3h. Subsequently, the mixture was again refluxed for 12h to complete the reaction. The salts were then separated by filtration. From the toluene solution colourless crystals of the heptaphosphane could be grown at -80°C. Yield: 85%.

$^{31}P$-NMR (Toluene): $\delta$ = -0.8 ppm (m, 3P), -98.8 ppm (m, 1P), -155.5 ppm (m, 3P)

$^{29}Si$-NMR (Toluene): $\delta$ = 7.2 ppm ($\mathit{Si}Me_3$), $^1J(SiP)$ = 39 ± 5 Hz.

### 4.6.2 Synthesis of $P_7[Si(SiMe_3)_3]_3$

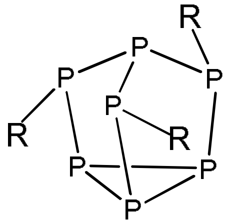
| | | | |
|---|---|---|---|
| K | 2.65 g | 39.10 $g.mol^{-1}$ | 67.81 mmol |
| Na | 2.12 g | 22.99 $g.mol^{-1}$ | 92.04 mmol |
| P | 9.14 g | 30.97 $g.mol^{-1}$ | 295.48 mmol |
| $ClSi(SiMe_3)_3$ | 55.00 g | 283.13 $g.mol^{-1}$ | 176.00 mmol |

In a dry 500 mL round bottom three-necked flask a liquid alloy was formed from sodium (2.65 g, 67.81 mmol) and potassium (2.12 g, 92.04 mmol) by gently heating. After cooling, this alloy was covered by dry DME and the solvent was heated to reflux temperature for 2 h. The colour of the solvent turned to deep blue. The mixture was cooled to room temperature and red phosphorus was added (9.14 g, 295.48 mmol). The mixture was again heated to reflux for 12h. DME was then removed from the yellowish-green suspension i.v. at ambient temperature, and the residue was suspended in 200 mL of toluene. Then a solution of $(SiMe_3)_3SiCl$ (176.00 mmol, excess 55.00 g) in 100 mL of toluene was added dropwise at room temperature over a period of 1h. The mixture was again refluxed for three hours to complete the reaction, and the salts were then separated by filtration. From the toluene solution colourless crystals of the heptaphosphane could be grown at -80°C. Yield: 70%.

$^{31}$P-NMR (Toluene): $\delta$ = -1.9 ppm (m, 3P), -100.8 ppm (m, 1P), -165.6 ppm (m, 3P)
$^{29}$Si-NMR (Toluene): $\delta$ = -7.8 ppm (*Si*$Me_3$)
$\delta$ = -92.5 ppm (*Si*$(SiMe_3)_3$), $^1J(SiP)$ = 99 ± 5 Hz.

### 4.6.3 Synthesis of $P_7[SiMe(SiMe_3)_2]_3$

$$3\ \mathrm{Na/K} \quad + \quad 7\mathrm{P} \quad + \quad 3\mathrm{ClR} \quad \xrightarrow[\mathrm{R= -SiMe(SiMe_3)_2}]{}$$



| | | | |
|---|---|---|---|
| K | 1.05 g | 39.10 $g.mol^{-1}$ | 26.97 mmol |
| Na | 0.84 g | 22.99 $g.mol^{-1}$ | 36.61 mmol |
| P | 3.62 g | 30.97 $g.mol^{-1}$ | 117.52 mmol |
| $ClSiMe(SiMe_3)_2$ | 20.00 g | 224.95 $g.mol^{-1}$ | 70.00 mmol |

In a dry 250 mL round bottom three-necked flask a liquid alloy was formed from sodium (0.84 g, 36.61 mmol) and potassium (1.05 g, 29.97 mmol) by gently heating. After cooling, this alloy was covered by dry DME and the solvent was heated to reflux temperature for 2 h. The colour of the solvent turned to a deep blue. After cooling to room temperature red phosphorus was added (3.62 g, 117.52 mmol) and the mixture was again heated to reflux for 36h. DME was then removed from the yellowish-green suspension by evaporation i.v. at ambient temperature. The phosphanide was suspended in about 100 mL of toluene. Then a solution of $(SiMe_3)_2MeSiCl$ (70.00 mmol, excess 20.00 g) in 50 mL of toluene was added dropwise at room temperature over a period of 1h. The mixture was again refluxed for three hours to complete the reaction. The salts were then separated by filtration. Colourless crystals could be grown at -80°C. Yield: 75%.

$^{31}$P-NMR (Toluene): δ = 0 ppm (m, 3P), -85 ppm (m, 1P), -167 ppm (m, 3P).

$^{29}$Si-NMR (Toluene): δ = -15.5 ppm (*Si*$Me_3$),

δ = -51.7 ppm (*Si*Me), $^1J(SiP)$ = 83.5 ± 5 Hz.

### 4.6.4 Synthesis of $(SiMe_3)_3SiH$ and $Si(SiMe_3)_4$

$$HSiCl_3 + 3Me_3SiCl + 6Li \longrightarrow (SiMe_3)_3SiH + Si(SiMe_3)_4 + 6LiCl$$

| | | | |
|---|---|---|---|
| Li | 100.00 g | 6.90 $g.mol^{-1}$ | 14.40 mol |
| $Me_3SiCl$ | 686.00 g | 108.60 $g.mol^{-1}$ | 6.30 mol |
| $HSiCl_3$ | 286.00 g | 135.50 $g.mol^{-1}$ | 2.10 mol |

In a 2L two necked flask with a reflux condenser, lithium (100.00 g, 14.40 mol ) was suspended in 1L THF. In a 2L dropping funnel, 280 mL of $HSiCl_3$ (2.10 mol) and 686 mL of $Me_3SiCl$ (6.30 mol) were mixed. The mixture was slowly added dropwise over a period of 4 hours under vigorous stirring at 0°C (ice bad) to the suspension of lithium. The reaction mixture turned gradually pale yellow to dark brown. After the addition of $HSiCl_3$ and $Me_3SiCl$, the reaction mixture was slowly allowed to come to room temperature and stirred overnight.

The diethyl ether solution was added into a mixture of 2M $H_2SO_4$ / diethyl ether, cooled to 0°C with an ice/water bath. Layers were separated. The aqueous layer was re-extracted two times with diethyl ether. The combined organic layers were dried over anhydrous $Na_2SO_4$. After filtration and removal of the solvent, the crude product consisting of $(SiMe_3)_3SiH$ and $(SiMe_3)_4Si$ was purified by fractional distillation ($(SiMe_3)_3SiH$) and sublimation ($(SiMe_3)_4Si$).

Yield: $HSi(SiMe_3)_3$ : 366 g, ~70%

bp: 50°C, 0.01 mbar

$^{29}$Si-NMR (Toluene): δ(H*Si*) = -115.5 ppm, δ(*Si*$Me_3$) = -12.3 ppm

Yield: $Si(SiMe_3)_4$ : 203 g (~30%)

$^{29}$Si-NMR (Toluene): δ(*Si*($SiMe_3$)) = -135,5 ppm, δ(*Si*$Me_3$) = -9,7 ppm

### 4.6.5 Synthesis of tris(trimethylsilyl)silane from $Si(SiMe_3)_4$

$$Si(SiMe_3)_4 + KO^tBu \longrightarrow KSi(SiMe_3)_3 + Me_3SiO^tBu$$

$$KSi(SiMe_3)_3 + H^+ \longrightarrow HSi(SiMe_3)_3 + K^+$$

| | | | |
|---|---|---|---|
| $Si(SiMe_3)_4$ | 14.1 g | 320.5 g.mol$^{-1}$ | 44.0 mmol |
| $KO^tBu$ | 5.3 g | 112.0 g.mol$^{-1}$ | 47.0 mmol |
| $H_2SO_4$ | 250.0 mL | 0.2 M | 50.0 mmol |

In a 100 mL two necked flask tetrakis(trimethylsilyl)silane (14.1 g, 44.0 mmol) was dissolved in 60 mL of THF. Potassium tert-butalonate (5.3 g, 47.0 mmol) was added with a spatula to the colourless solution. The reaction mixture was stirred overnight, and the colour of the solution turned dark green. The THF solution was transferred in a dropping funnel and added dropwise to a solution of 0.2 M $H_2SO_4$ in a 250 mL two necked flask. After 2h the two layers were separated, and the aqueous layer was re-extracted two times with diethyl ether. The combined organic layers were dried over anhydrous $Na_2SO_4$ and after filtration and removal of solvent the crude product was purified by vacuum distillation.

Yield: 10.9 g (100%)

### 4.6.6 Synthesis of chlorotris(trimethylsilyl)silane (HypCl) [113]

$$HSi(SiMe_3)_3 + CCl_4 \longrightarrow ClSi(SiMe_3)_3 + HCCl_3$$

| | | | |
|---|---|---|---|
| $HSi(SiMe_3)_3$ | 10.9 g | 286.5 g.mol$^{-1}$ | 44.0 mmol |
| $CCl_4$ | 100.0 g | 126.13 g.mol$^{-1}$ | 0.7 mol |

Tris(trimethylsilyl)silane (44.0 mmol, 44.0 mmol) was dissolved in $CCl_4$ (100.0 g, 0.7 mol) in a 250 mL three necked flask with reflux system. The solution was stirred under reflux overnight. The solvent was then removed and the crude product was purified by vacuum distillation.

Yield: 11.2 g, 90%
Bp: 40°, 0.01 mbar

$^{29}$Si-NMR (Toluene): δ = -14.7 ppm (*Si*($SiMe_3$)$_3$)
δ = -11.5 ppm. (*Si*$Me_3$)

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[113] Brook, A. G; Yau, L.; *J. Organomet. Chem.* **1984**, 271(1-3), 9.

### 4.6.7 Synthesis of $[Me_3Si]_3SiSiMe_2H$

$$Si(SiMe_3)_4 + KO^tBu \longrightarrow KSi(SiMe_3)_3 + Me_3SiO^tBu$$

$$KSi(SiMe_3)_3 + Me_2SiHCl \longrightarrow [Me_3Si]_3SiSiMe_2H + KCl$$

| | | | |
|---|---|---|---|
| $Si(SiMe_3)_4$ | 50.7 g | 320.50 $g.mol^{-1}$ | 158.0 mmol |
| $KO^tBu$ | 17.7 g | 112.00 $g.mol^{-1}$ | 158.0 mmol |
| $Me_2SiHCl$ | 15.0 g | 94.61 $g.mol^{-1}$ | 158.0 mmol |

In a 500 mL two necked flask tetrakis(trimethylsilyl)silane (50.7 g, 158.0 mmol) was dissolved in 250 mL of THF. Potassium tert-butalonate (17.7 g, 158.0 mmol) was added with a spatula to the colourless solution. The reaction mixture was stirred over night. The colour turned dark green. The THF was removed by evaporation i.v. and 250 mL of dry toluene was added. The solution was transferred in a dropping funnel and added dropwise to a toluene solution of $Me_2SiHCl$ (15.0g, 158.0 mmol). The resulting mixture was stirred for one day. The mixture was then filtrated and the solvent was removed under vacuum. The sticky white solid obtained was sublimed (53°C, 2 Torr) to give (dimethylsilyl)tris(trimethylsilyl)silane as a colourless crystalline solid.

Yield: 29 g, 60%

$^1$H-NMR ($C_6D_6$): δ(H, s, $SiMe_3$) = 0.20 ppm,
δ(H, d, $SiMe_2$) = 0.27 ppm $^3J(SiMe_2)$= 4.4 Hz
δ(H, SiH) = 4.02 ppm

$^{29}$Si-NMR ($C_6D_6$): δ(*Si*$Me_3$) = -9.7 ppm
δ(*Si*$Me_2$H) = -33.6 ppm
δ(*Si*($SiMe_3$) = -136.8 ppm

### 4.6.8 Synthesis of $[Me_3Si]_3SiSiMe_2I$

$$[Me_3Si]_3SiSi(Me_3)_2H + \text{ excess } HCI_3 \longrightarrow [Me_3Si]_3SiSi(Me_3)_2I$$

| | | | |
|---|---|---|---|
| $[Me_3Si]_3SiSiMe_2H$ | 29.0 g | 306.8 $g.mol^{-1}$ | 94.0 mmol |
| $CH_3I$ | 74.0 g | 393.71 $g.mol^{-1}$ | 188.0 mmol |

In a 100 mL two necked flask (dimethylsilyl)tris(trimethylsilyl)silane (29.0 g, 94.0 mmol) was dissolved into 150 mL heptane. Iodoform (74.0 g, 188.0 mmol) was added with a spatula to the colourless solution. The reaction mixture was stirred for 10 days. The colour of the solution turned brown. After removal of the solvent and unreacted iodoform under reduced pressure, the brown solid obtained was rinsed several times by $CH_2Cl_2$ to leave a pale brown solid which was purified by sublimation (70°C, 0.02 mm Hg).

Yield: 28 g, 70%

$^1$H-NMR ($C_6D_6$): δ(27 H, s, $SiMe_3$) = 0.27 ppm
δ(6H, $SiMe_2I$) = 0.93 ppm

$^{29}$Si-NMR ($C_6D_6$): δ(*Si*$Me_3$) = -9.45 ppm
δ(*Si*$Me_2I$) = -58.3 ppm
δ(*Si*($SiMe_3$) = -126.3 ppm

### 4.6.9 Synthesis of Methyltris(trimethylsilyl)silane

$$2\,(Me_3Si)_3SiK \;+\; Me_2SO_4 \xrightarrow{THF} 2\,(Me_3Si)_3SiMe \;+\; K_2SO_4$$

| | | | |
|---|---|---|---|
| $KSi(SiMe_3)_3$ | 18.98 g | 248.0 $g.mol^{-1}$ | 66.2 mmol |
| $Me_2SO_4$ | 5.84 g | 152.0 $g.mol^{-1}$ | 46.3 mmol |

To a solution of dimethylsulfate (5.84 g, 46.3 mmol) in THF, a solution of tris(trimethylsilyl)silyl potassium (18.98 g, 66.2 mmol) was added dropwise at 0°C over a period of 1h. The dark red colour disappeared immediately and the formation of a white precipitate was observed. The reaction mixture was warmed up to room temperature, and was added to a mixture of 2M $H_2SO_4$ / diethyl ether, cooled to 0°C with an ice/water bath. Layers were separated, and the aqueous layer was re-extracted two times with diethyl ether. The combined organic layers were dried over anhydrous $Na_2SO_4$, and after filtration and removal of the solvent, the crude product was purified by vacuum distillation (55°C, 0.05 mm Hg).

Yield: 11g, 60%

$^1$H-NMR ($C_6D_6$): δ(s, 1H, Me) = 0.11 ppm; δ(s, 27H, $SiMe_3$) = 0.20 ppm.

$^{29}$Si-NMR ($C_6D_6$): δ(*Si*Me) = -88.0 ppm
δ(*Si*$Me_3$) = -12.3 ppm.

### 4.6.10 Synthesis of chloromethylbis(trimethylsilyl)silane from $(SiMe_3)_3SiMe$

$$(SiMe_3)_3SiMe + PCl_5 \longrightarrow (SiMe_3)_2Si(Me)Cl + ClSiMe_3 + PCl_3$$

| | | | |
|---|---|---|---|
| $(SiMe_3)_3SiMe$ | 49.21 g | 262.70 g.mol$^{-1}$ | 187.30 mmol |
| $PCl_5$ | 39.00 g | 207.40 g.mol$^{-1}$ | 188.00 mmol |

In a 250 mL three necked flask with a reflux condenser, methyltris(trimethylsilyl)silane (49.21 g, 187.30 mmol) was dissolved in 150 mL of DME. $PCl_5$ (39.00 g, 188.00 mmol) was added with a spatula to the solution under vigorous stirring. The solution warmed up due to the addition of $PCl_5$. The reaction was kept to reflux temperature for two days. The solvent was removed under reduced pressure, and the crude product was purified by fractional distillation.

Yield: 33.7 g, 80%
Bp: 55°C, 0.05 mm Hg
$^{29}$Si-NMR ($C_6D_6$): δ(*Si*MeCl) = -9.6 ppm
δ(*Si*Me$_3$) = -15.0 ppm.

# 5 Summary

Heptaphosphanes $P_7R_3$ (with R = $SiMe_3$, $SiMe(SiMe_3)_2$, $Si(SiMe_3)_3$) could be synthesized from red phosphorus, sodium/potassium alloy and a suitable chlorooligosilane $ClR_3$.

Depending of the size of the substituent, one SiP bond or one SiSi bond was cleaved by $KO^tBu$ or $LiO^tBu$. When R was the trimethylsilyl group $SiMe_3$, the use of one equivalent of $KO^tBu$ or $LiO^tBu$ led to the heptaphosphanides $[P_7R_2]^-$. With $LiO^tBu$, concomitant inversion at an equatorial silylated phosphorus atom occurred and the $C_s$ symmetric isomer characterized by a mirror plane was formed. With $NaO^tBu$ a mixture of both isomers was obtained. The hexacosaphosphanide $[P_{16}]^{2-}$ could be synthesized in one step using two equivalents of $KO^tBu$. When R was the hypersilyl group $Si(SiMe_3)_3$, the SiP bonds were shielded very effectively, and a trimethylsilyl group was cleaved off by $KO^tBu$ forming $[Hyp_2P_7(Si(SiMe_3)_2)_2]^-K^+$. With $LiO^tBu$, only SiP bonds were cleaved, and the heptaphosphanide $[P_7R_2]^-Li^+$ was formed. However, $[P_7R_2]^-K^+$ could be obtained by action of $KO^tBu$ on $(SiMe_3P_7[Si(SiMe_3)_3]_2$.

The anions $[P_7R_2]^-$ (with R= $SiMe_3$, $Si(SiMe_3)_3$) were stable and could be used as valuable synthons for further reactions. The reaction of $KP_7(SiMe_3)_2$ or $LiP_7(SiMe_3)_2$ with 1,2-dichlorotetramethyldisilane led to $(SiMe_3)_2P_7SiMe_2SiMe_2P_7(SiMe_3)_2$. The reaction between $KP_7[Si(SiMe_3)_3]_2$ or $LiP_7[Si(SiMe_3)_3]_2$ and $CF_3CO_2H$ formed $HP_7[Si(SiMe_3)_3]_2$. But many reactions of $[P_7R_2]^-$ were unsuccessful, and led to the complete degradation of the $P_7$-backbone.

In order to functionalize the heptaphosphanes, the silyl exchange between $-SiMe_3$ substituent of $P_7(SiMe_3)_3$ and a bulky oligosilyl group turned out to be a good pathway for the synthesis of novel heterolepticaly substituted heptaphosphanes. The use of this method allowed the one step synthesis of $P_7R_2R'$, for instance $SiMe_3P_7[Si(SiMe_3)_3]_2$ and $SiMe(SiMe_3)_2P_7[Si(SiMe_3)_3]_2$. Starting from $P_7(SiMe_3)_3$ it allowed also the formation of the cages of the type $P_7R_3$, such as $P_7(Si_6Me_{11})_3$. Two cages could also be bridged by this method, with the formation of $(SiMe_3)_2P_7SiMe_2SiMe_2P_7(SiMe_3)_2$ using $ClSiMe_2SiMe_2Cl$. The driving force of the silyl exchange was the stabilization of the $P_7$-cage by the larger silyl-substituent. This method could be a valuable method for the synthesis of many other heptaphosphanes $P_7R_2R'$ starting from $P_7(SiMe_3)$.

The heteroleptically substituted heptaphosphane $SiMe_3P_7[Si(SiMe_3)_3]_2$ was easily synthesized via silyl exchange between $P_7(SiMe_3)_3$ and $ClSi(SiMe_3)_3$. Because it bears two different size demanding substituents, it was a useful reagent for this work. It allowed the one step synthesis of $HP_7[Si(SiMe_3)_3]_2$ by action of an alcohol (here MeOH or $^t$BuOH), and formation of $ClSi_2Me_4P_7[Si(SiMe_3)_3]_2$ and $ClSnPh_2P_7[Si(SiMe_3)_3]_2$ by action of $ClSi_2Me_4Cl$ and $Cl_2SnPh_2$, respectively.

The first heteroleptically substituted heptaphosphanes bearing a halogen atom, $R_2P_7X$ (with X = Cl, Br, I and R = $Si(SiMe_3)_3$), were synthesized in the reaction of $SiMe_3P_7[Si(SiMe_3)_3]_2$ and $Br_2C_2Cl_4$, $C_2Cl_6$ and $I_2$.