Synthesis of novel silicon-phosphorus rings and cages

Dissertation of Ana Rodrigues

Carried out under supervision of Prof. Dr. Karl Hassler at the Institute of Inorganic Chemistry, TU Graz, from March 2008 to June 2011.

"Há um tempo em que é preciso abandonar as roupas usadas, que já tem a forma do nosso corpo e esquecer os nossos caminhos, que nos levam sempre aos mesmos lugares. É o tempo da travessia: e, se não ousarmos fazê-la, teremos ficado para sempre, à margem de nós mesmos."

By Fernando Pessoa

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Obrigada por tudo!

Thank you for everything!

Synthese neuer Silizium-Phosphor Ringe und Käfige

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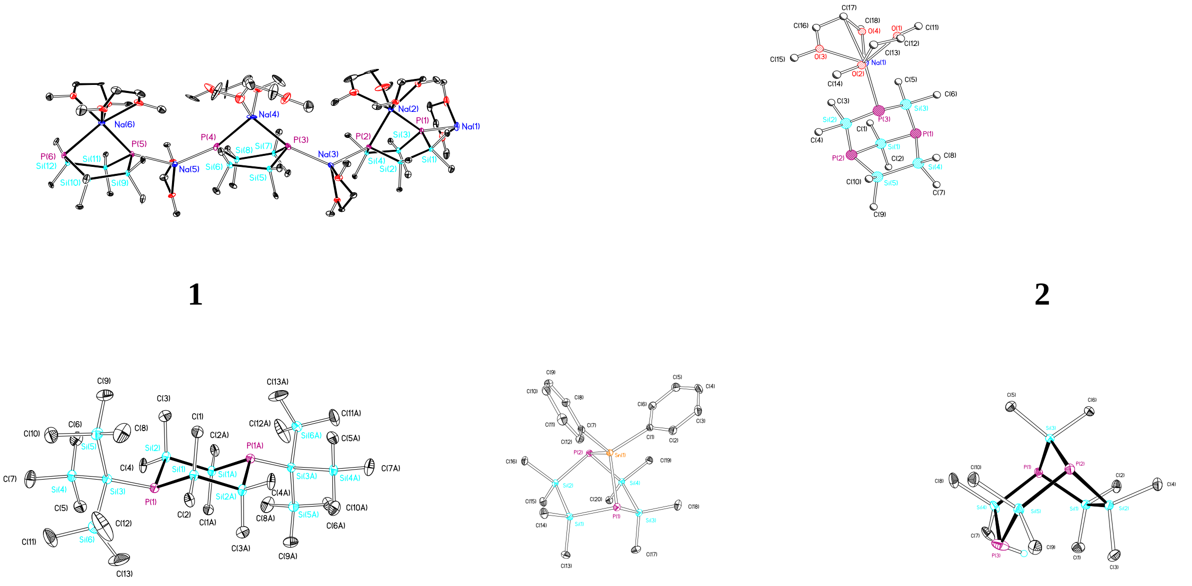
Die Tendenz der Elemente Silizium und Phosphor, Ringe und Käfige zu bilden ist bekannt und wurde in der Vergangenheit ausgiebig diskutiert[1], [2]. Die Reaktion von 1,2-Dichlortetramethyldisilan mit Natrium-Kalium-Phosphanid (hergestellt aus den Elementen in DME) liefert verschiedene anionische Ringsysteme wie $[(Me_4Si_2)_2P_2]^{2-}$ **1,** und $[(Me_5Si)_5P_3]^-$ **2,** indem einfach die Menge an zugesetztem 1,2-Dichlortetramethyldisilan verändert wird.

Ausgehend von **1** und **2**, wurden $[[(Si(SiMe_3)_3]_2(Me_4Si_2)_2P_2]$ **3**, $P_2Si_4Me_8SnPh_2$ **4** und $[(Me_2Si)_5P_3H]$ **5** dargestellt. **3**, **4** und **5** wurden mittels ^{29}Si-und ^{31}P-NMR-Spektroskopie charakterisiert. Die Kristallstrukturen wurden durch Röntgenstrukturanalyse aufgeklärt.



1 **2**

3 **4** **5**

Figure 1: Molekulstrukturen von **1**, **2** , **3, 4** und **5**.

Literatur

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[2]. G.M. Kollegger, U. Katzenbeisser, K. Hassler, C. Krüger, D. Brauer, R. Gielen, J. Organomet. Chem. 1997, 543, 103.

Synthesis of novel silicon-phosphorus rings and cages

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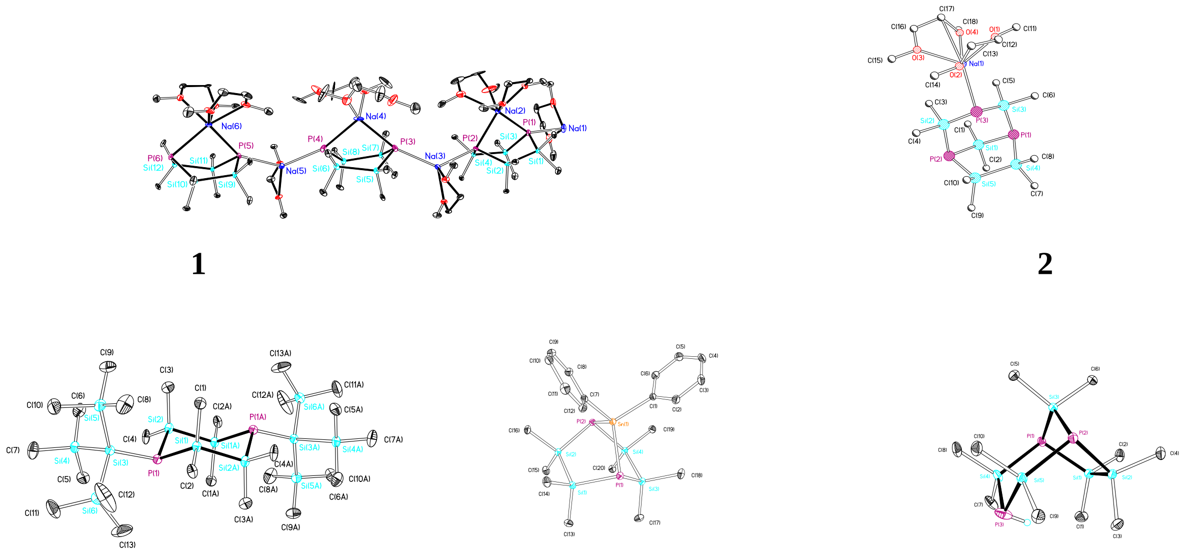
The tendency of the elements silicon and phosphorus to form rings and cages is known and has been reviewed extensively in the past [1], [2]. The reaction of 1,2-dichlorotetramethyldisilane with sodium potassium phosphanide (prepared from the elements in DME) provides different anionic ring systems such as $[(Me_4Si_2)_2P_2]^{2-}$ **1,** and $[(Me_5Si)_5P_3]^-$ **2,** simply by changing the amount of 1.2-dichlorotetramethyldisilane added.

From **1** and **2**, $[[(Si(SiMe_3)_3]_2(Me_4Si_2)_2P_2]$ **3**, $P_2Si_4Me_8SnPh_2$ **4** and $[(Me_2Si)_5P_3H]$ **5**, can be formed respectively. **3**, **4** and **5** were characterized by ^{29}Si and ^{31}P-NMR spectroscopy. The crystal structures have been elucidated by X-ray crystallography.



1 **2**

3 **4** **5**

Figure 1: Molecular structures of **1**, **2**, **3, 4** and **5**.

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[1]. G. Tekautz, J. Baumgartner, A.Dransfeld, K.Hassler, Eur. J. Inorg. Chem.. 2007, 4071-4077.

[2]. G.M. Kollegger, U. Katzenbeisser, K. Hassler, C. Krüger, D. Brauer, R. Gielen, J. Organomet. Chem. 1997, 543, 103.

1- Introduction

Since the first synthesis of H_3Si-PH_2 by Fritz and co-workers over 50 years ago, the field of molecular compounds with Si-P bonds has been of ongoing interest. Quite a number of rings and cages consisting of an alternating arrangement of P and Si atoms have been described. The tendency of these elements to form rings and cages is well known, these compounds show an extensive structural chemistry and are excellent starting compounds for the synthesis of different phosphorus bridged complexes of main group and transition metals.

Most of the species known so far exhibit an alternating sequence of silicon and phosphorus atoms, silylphosphanes with disilane bridges between phosphorus atoms are still rare.

The reaction which has been used most frequently for the preparation of these compounds is the salt elimination from a phosphanide and a silicon halide, usually a silicon chloride.

The aim of this thesis was the synthesis of novel anionic silicon-phosphorus rings and cages using a more simple and convenient way, using the reaction of 1,2-dichlorotetramethyldisilane with sodium potassium phosphanide (prepared from the elements in DME) by changing the amount of 1.2-dichlorotetramethyldisilane added.

The second aim was to study the reactivity of the anionic systems obtained.

2- Literature overview

2.1- Silylphosphanes

2.1.1- Formation of silicon-phosphorus bonds

The first compounds of this class, $(SiH_3)_3P$ was prepared by Aylett, Emeleus and Maddock[1], by the reaction of white phosphorus with iodosilane. Subsequently silylphosphane $SiH_3PH_2$was synthesized by Fritz[2]. This substance is formed at 450 ° C in the gas phase from SiH_4 and PH_3. In the IR-spectrum a band at 454cm^{-1} was assigned the Si-P bond stretching vibration[3].

Apart from thermal gas phase reactions silylphosphanes were also prepared by electrical discharges in gas mixtures of silanes and phosphanes. SiH_3PH_2[4], $(SiH_3)_2PH$[5] and $Si_2H_5PH_2$[6] could be synthesized by this method.

The handling of this very sensitive substance is extremely difficult and the implementation of gas-phase reactions in the lab is not very pleasant.

The reaction used more frequently for the preparation of this compound is the salt elimination from a phosphanide and a silicon halide, usually a silicon chloride.

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[1] Aylett, B.J; Emeleus, H.J.; Maddock, A.G.; Research (London), **1953**, 6, 30.

[2] Fritz, G., Z. Natruforsch., **1953**, 8b, 776.

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The first such reaction, which should turn out later as a universal method, was used by Kuchen and Buchenwald to prepare trimethylsilyldiphenylphosphane[7], in the reaction of diphenylsodiumphosphanide and trimethylchlorosilane. The desired product formed in more than a sixty percent yield (Figure 1).

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

Figure 1: Synthesis of trimethylsilyldiphenylphosphane.

Difficulties arise with this method as soon as there are more than one functional groups. Thus, the reaction between bromosilane with potassiumphosphanide does not give the expected silylphosphane H_3SiPH_2 but instead $P(SiH_3)_3$. It is formed by transmetalation[8].

Lithiumdiethyl phosphanide proved subsequently to be a suitable reagent to form silylphosphanes[9] from polyfunctional silanes.

With an excess of lithium phosphanide lithiation of the Si- atom is possible.

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

$$H_2Si(PEt_2)_3 \quad + \quad LiPEt_2 \longrightarrow LiSi(PEt_2)_2 \quad + \quad HPEt_2$$

Figure 2: Multiple functionalization of silylphosphanes.

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[7] Kuchen, W.; Buchenwald, K.; Angew. Chem., **1957**, 69, 307.

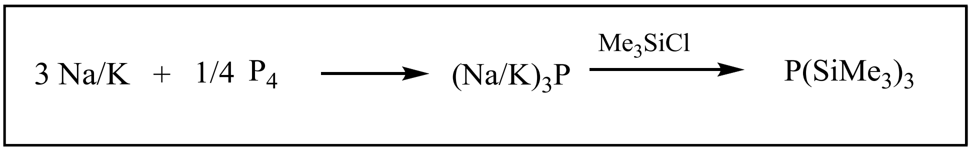
[8] Amberger, E.; Boeters, H.G.; Angew. Chem., **1962**, 74, 32.

[9] Fritz, G.; Becker, G.; Z. Anorg. Allg: Chem.,**1970**, 372, 180.

Silylphosphanes can also be synthesized by starting from elemental phosphorus.

The first step is the formation of sodium/potassium alloy to which elemental phosphorus is added to obtain a ''Zintl'' phase. A chlorosilane is then added to the mixture so that the desired product is formed.

A typical example for this pathway is the formation of tris(trimethylsilyl)phosphane (Figure 3).[10]



$$3\ \mathrm{Na/K} + 1/4\ \mathrm{P_4} \longrightarrow (\mathrm{Na/K})_3\mathrm{P} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{P(SiMe_3)_3}$$

Figure 3: Synthesis of tris(trimethylsilyl)phosphane starting from elemental phosphorus.

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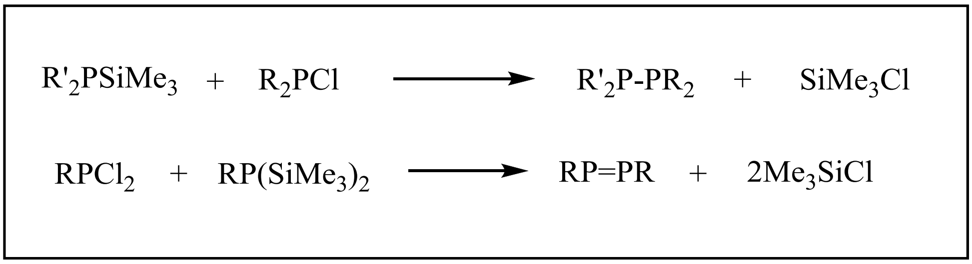
[10] Karsch, H.; Bienlein. F.; Rupprich, T.; Uhlig, F.; Herrman, E.; Scheer, M.; Synthetic Methods of Organometallic and Inorganic Chemistry, (Ed. Karsch, H.H.), Thieme, Stuttgart, **1996**, 3, 58.

2.1.2- Use of silylphosphanes for phosphorus - phosphorus bond formation

There are several possibilities to build longer phosphorus chains substituted with silyl groups, for instance by reacting a phosphanide with a halophosphane[11, 12, 13.] Other possibilities are the coupling of phosphanides by dibromoethane[14] or a silicon - phosphorus bond cleavage by PR_2Cl, forming P-P single and double bonds (Figure 4)[15].



$$R'_2PSiMe_3 + R_2PCl \longrightarrow R'_2P\text{-}PR_2 + SiMe_3Cl$$

$$RPCl_2 + RP(SiMe_3)_2 \longrightarrow RP{=}PR + 2Me_3SiCl$$

Figure 4: Possibilities for the formation of PP bonds in silylated phosphanes (R = organyl, silyl).

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[11] Baudler, M.; Hallb, M.; Zarkadas, A.; Chem. Ber., **1973**, 106, 3962.

[12] Höfler, F.; Wolfer D.; Hengge, E.; Top.Curr. Chem., **1974**, 51, 87.

[13] Fritz, G.; Vaahs, I.; Härer, J.; Z.Anorg. Allg. Chem., **1987**, 552, 11.

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

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

2.1.3- Functionalization of silylphosphanes

To carry out further reactions with silylphosphanes, it is advantageous to introduce functional silyl groups into the molecule.

However functionalization of silylphosphanes at the Si-atom without a cleavage of a SiP bond is difficult to do.

By disproportionation silylphosphanes with hydrogen and halogen on silicon are accessible as shown in Figure 5[16].

$$3\ H_2ClSiPEt_2 \longrightarrow 2\ H_3SiPEt_2 + Cl_3SiPEt_2$$

$$H_3SiPEt_2 + Cl_3SiPEt_2 \longrightarrow H_3SiCl + Cl_2Si(PEt_2)_2$$

Figure 5: Disproportionation of halogenated silylphosphanes.

Silylated phosphanides are quite easily accessible, for instance by phosphorus - silicon bond cleavage using R-Li or R-Na (Figure 6). Another second bond cleavage does not occur easily. However, this reaction proceeds only in polar solvents such as ethers. Under ether-free conditions, no phosphorus - silicon bond is attacked (Figure 6)[17].

$$P(SiMe_3)_3 + nBuLi \longrightarrow LiP(SiMe_3)_2.DME + Me_3SiBu$$

$$HP(SiMe_3)_2 + nBuLi \longrightarrow LiP(SiMe_3)_2 + Me_3SiH$$

Figure 6: Reaction of silylphosphanes with butyllithium.

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[16] Fritz, G.; Becker, G.; Z. Anorg. Allg. Chem., **1970**, 372, 104.

[17] Fritz, G., Hölderlich, W.; Z. Anorg. Allg. Chem., **1976**, 422, 104.

Silicon - phosphorus bond cleavage can also occur with tertiary alkoxides, such as ^{t}BuOK.

R_2PH can also be metalated with NaH, KH, or with an alkalil metal in polar solvents[18].

In addition, these compounds can be also metalated with lithium (Figure 7). In this way, dilithiated species are prepared. By changing the phosphanide used for the lithiation the reaction can be controled and the –PHLi group is accessible.

$$H_{3-x}Me_xSiPH_2 + 2\ LiPEt_2 \longrightarrow H_{3-x}Me_xSiPLi_2 + 2\ HPEt_2$$

$$H_{3-x}Me_xSiPH_2 + LiPHMe \longrightarrow H_{3-x}Me_xSiPHLi + MePH_2$$

Figure 7: Lithiation of PH functions in silylphosphanes.

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[18] Ulig, F.; Gremler, S.; Dargatz, M.; Scheer, M.; Herrmenn, E.; Z. Anorg. Allg. Chem., **1991**, 606, 105.

2.1.4- Linking phosphorus atoms by a silyl or alkyl bridge

A reaction between $LiP(SiMe_3)_2$ and dimethyldichlorosilane is shown in Figure 6. Depending 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[19].

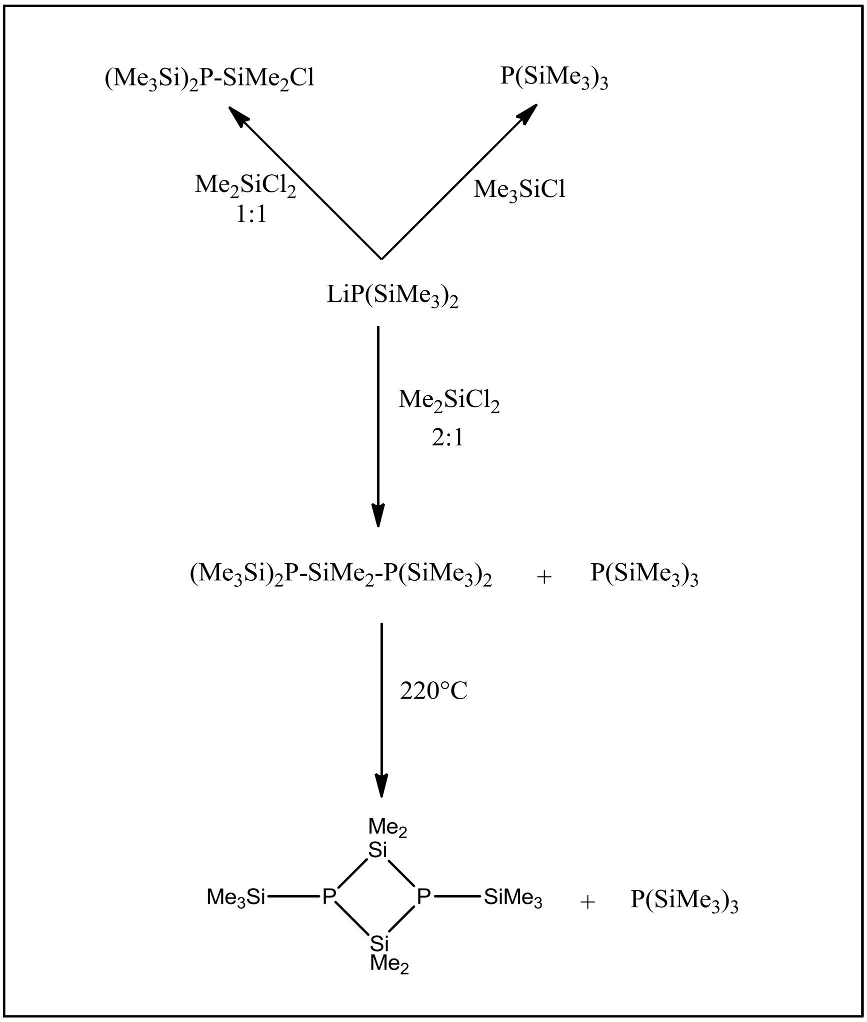

Figure 8: Reactions between $LiP(SiMe_3)_2$ and dimethyldichlorosilane.

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

The reaction of $LiP(Si^tBu_2)_2PH$ with an excess of Me_2SiCl_2 led to $HP(Si^tBu_2)_2PsiMe_2Cl$[20]. The same reaction in a molar ratio 2:1 gave $HP(Si^tBu_2)_2PSiMe_2P(Si^tBu_2)2PH$[21] (Figure 9).

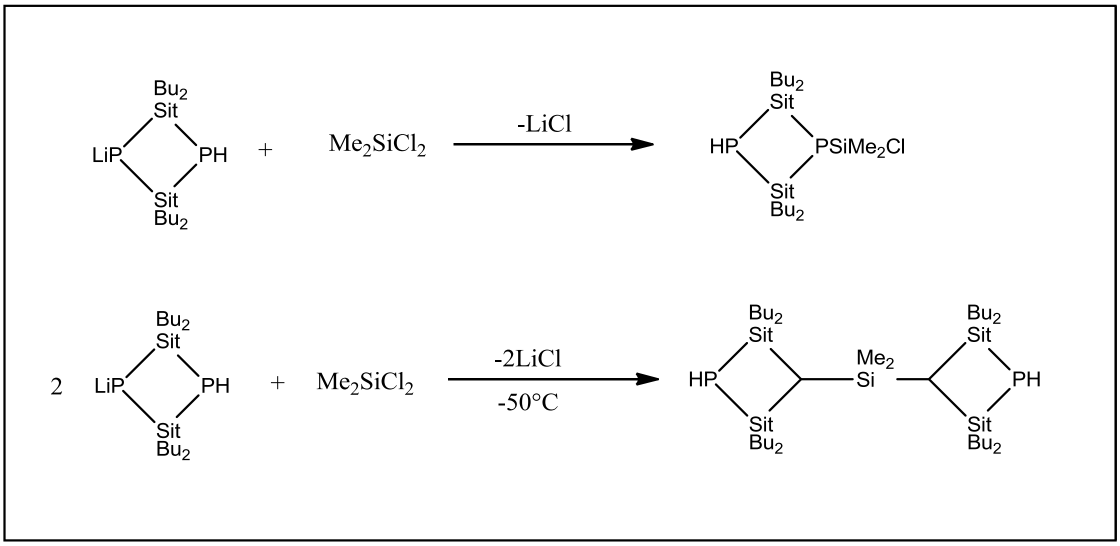

Figure 9: Reaction of $LiP(Si^tBu_2)_2PH$ with an excess of Me_2SiCl_2.

Another interesting result is the formation of tetrakis(trimethylsilyl)diphosphane from $LiP(SiMe_3)_2$ and $HgCl_2$ showed in Figure 10[22].

$$LiP(SiMe_3)_2 \;+\; HgCl_2 \longrightarrow (Me_3Si)_2P\text{-}P(SiMe_3)_2 \;+\; P(SiMe3)3 \;+\; LiCl \;+\; Hg$$

Figure 10: Formation of tetrakis(trimethylsilyl)diphosphane.

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

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

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

The use of various chlorinated hydrocarbons as shown below is also a good method to bridge two P-atoms[23, 24].

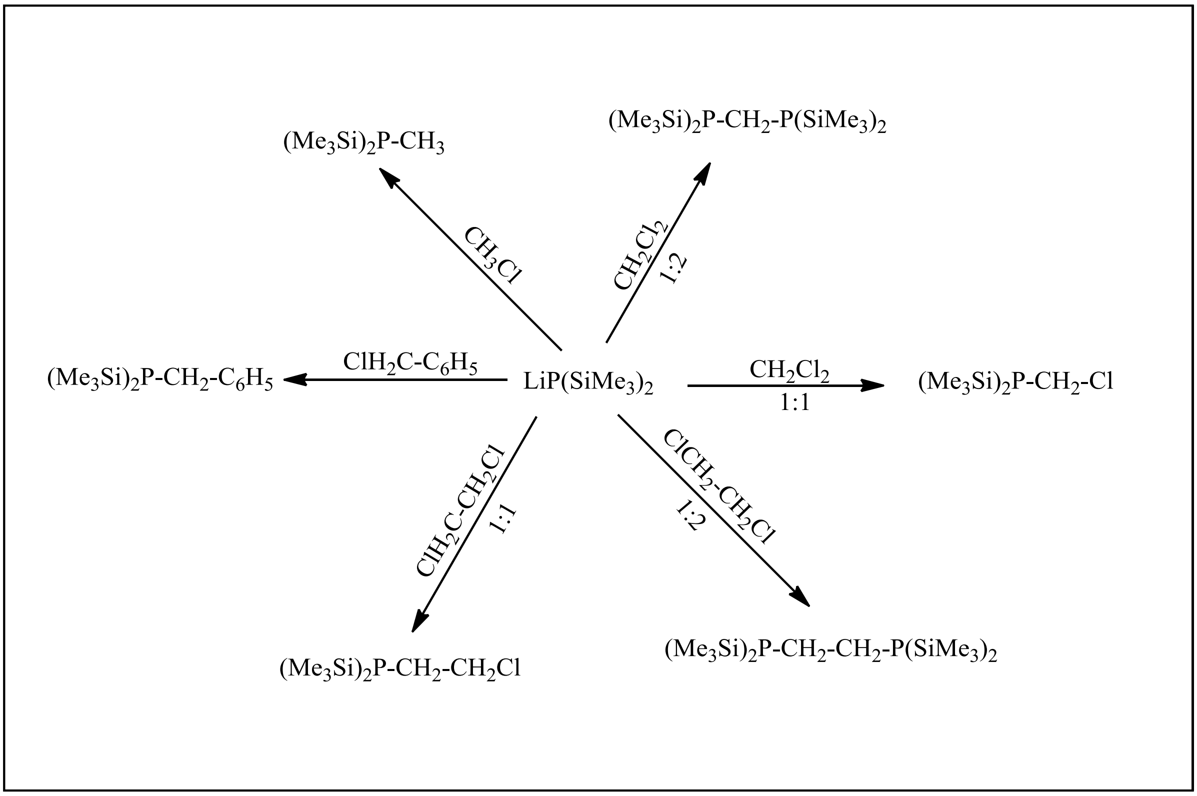

Figure 11: Synthetic pathways for bridging P-atoms.

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

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

2.1.5- Cyclic and polycyclic silylphosphanes

The above mentioned reactions can also be used to prepare cyclic or polycyclic compounds.

One possibility is to use multiply metalated phosphanides and react them with dihalosilanes. The first cage synthesized by this way was reported in 1959 (Figure 12)[25].

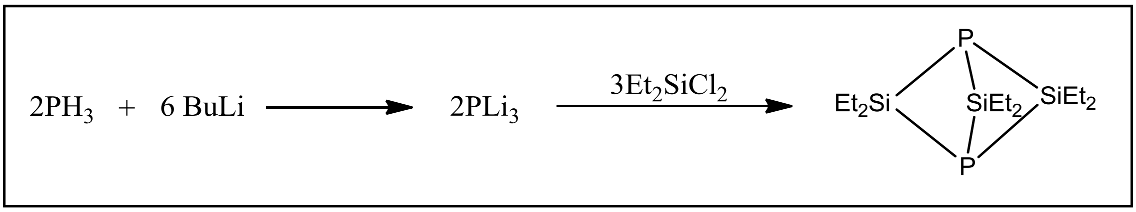

Figure 12: First phosphorus - silicon polycycle.

It was found that the bulkiness of the substituents affects the ring formation (Figure 13 (a))[26], as well as different temperatures. Higher temperatures favor larger rings (Figure 13 (b))[27].

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[25] Parshall, G.W.; Lindsey, R.V; J. Am. Chem. Soc.; **1959**, 81, 6237.

[26] Baudler, M.; Scholtz, G.; Tebbe, K.F; Feher, M.; Angew.Chem.,**1989**, 101, 352.

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

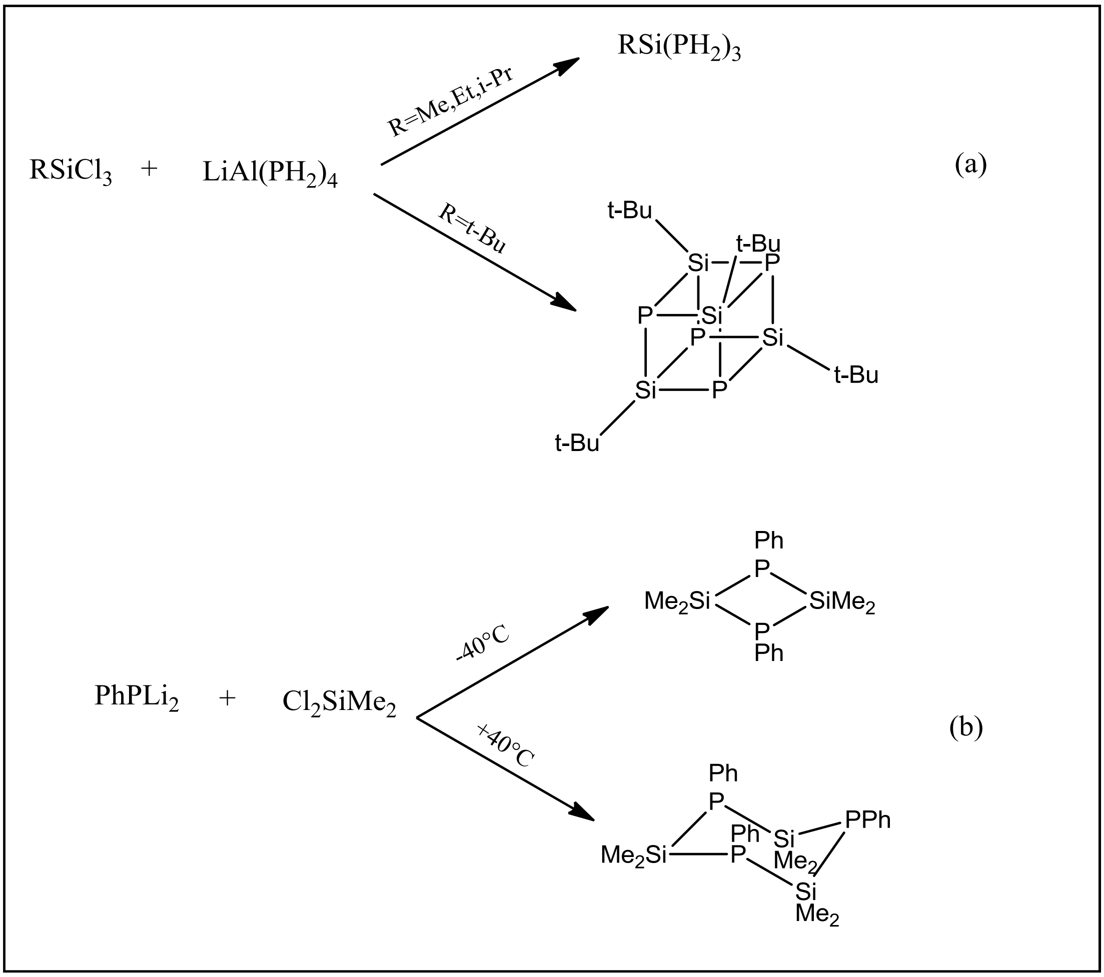

Figure 13: Influence of the substituent size (a), and the temperature (b) on the ring size.

Closer investigation revealed that the groups RHPLi or H_2PLi are capable to form rings. The proposed mechanism involves lithium - hydrogen exchange as a driving force for ring formation.

A compilation of the resulting cyclic and polycyclic compounds by reacting $LiPH_2$, LiPH and LiP with Me_2SiCl_2 is shown in Figure 14[28].

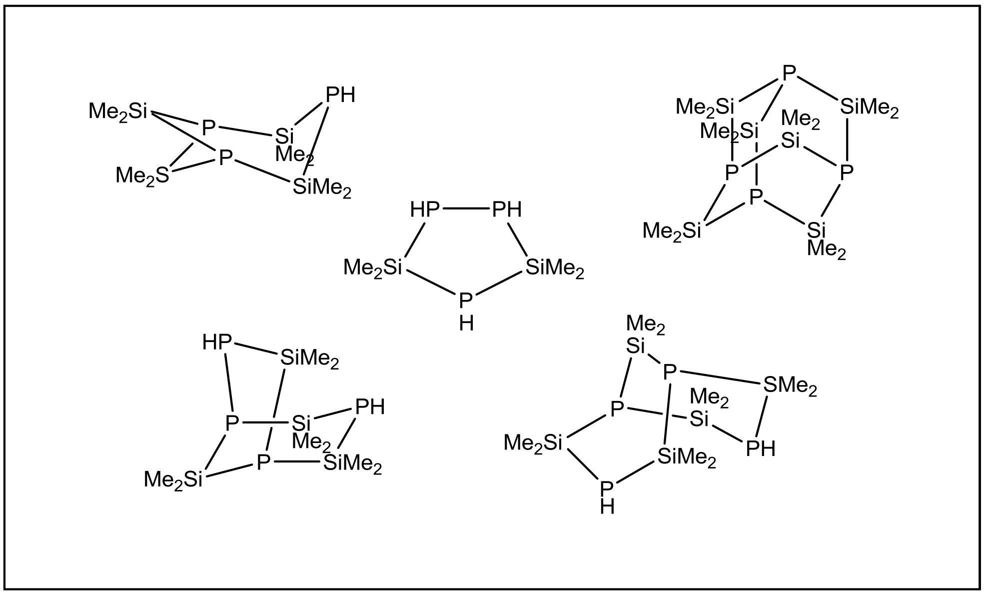

Figure 14: Cyclic products in the reaction of Me_2SiCl_2 with lithiumphosphanide.

$P_4(SiMe_2)_6$ with an adamantane backbone is the main product as it is thermally most stable. Moreover $P_4(SiMe_2)_6$ forms by thermal decomposition of suitable silylphosphanes[29].

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[28] Fritz, G.; Biastoch, R.; Z. Anorg. Allg. Chem., **1986**, 535, 63.

[29] Fritz, G.; Uhlmann, R.; Hölderlich, W.; Z. Anorg. Allg. Chem., **1987**, 442, 168.

Another way to prepare polycyclic phosphanes and silylphosphanes is the reaction of sodium / potassium phosphanides with chlorosilanes.

In this way, Si-P cages can be formed as can be seen in Figure 15[30, 31, 32, 33].

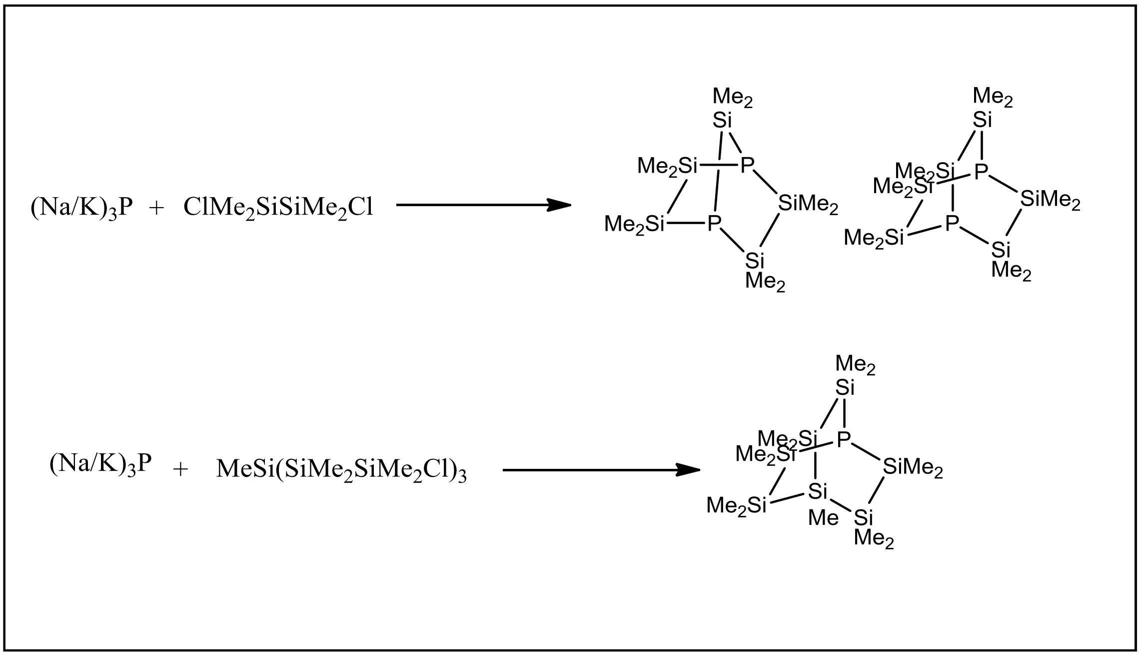

Figure 15: Preparation of some phosphorus - silicon cages.

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[30] Hassler, K.; J. Organomet. Chem., **1983**, 246, C31.

[31] Kolleger, G. M.; Katzenbeisser, U.; Hassler, K.; Krüger, C.; Brauer, D.; Gielen, R.; J. Organomet. Chem., **1997**, 543, 103.

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3- Results and discussion

3.1- Reactions with $P(Na/K)_3$

The tendency of the elements silicon and phosphorus to form rings and cages is known and has been reviewed extensively in the past. The reaction of 1,2-dichlorotetramethyldisilane with sodium/potassium phosphanide (prepared from the elements in DME) provides different anionic ring systems simply by changing the amount of 1,2-dichlorotetramethyldisilane added. As we will see in this chapter, this is a very sensitive reaction and also changing the reaction conditions can lead to a different result.

3.1.1- Synthesis of $[P_2Si_4Me_8]^{2-}$

$[P_2Si_4Me_8]^{2-}2Li^+$ is already known, the preparation of the dianion is long and not simple[34].

Quite a number of reactions were performed, and we could confirm that the product distribution in reactions between sodium/potassium pnictides and halogenated silanes strongly depends on the reaction conditions. In polar solvents as dimethoxyethane (DME), Si-Si bonds of the silane are easily broken. In these reactions considerable quantities of polymers are also formed. Up to now, there are no experimental studies on the influence of the solvent and the pnictogen/alkali metal ratio on the products of these reactions. The mechanisms of these reactions are not known. When $P(Na/K)_3$ reacts with 1,2-dichlorotetramethyldisilane many different cages can be formed depending on the reaction condition.

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[34] Hänisch. C.; Matern. E.; Z. Anorg. Allg. Chem., **2005**, 631, 1655.

The first reaction with P(Na/K)$_3$ was with the purpose to synthesise the dianion $[P_2Si_4Me_8]^{2-}$. In this reaction 30g of $Cl_2Si_2Me_4$ (one equivalent) was added dropwise to a suspension of P(Na/K)$_3$ in DME at -50°C over a period of 1h. After warming up to room temperature, the ^{31}P-NMR spectrum of the solution showed the presence of a mixture of compounds (Figure 16).

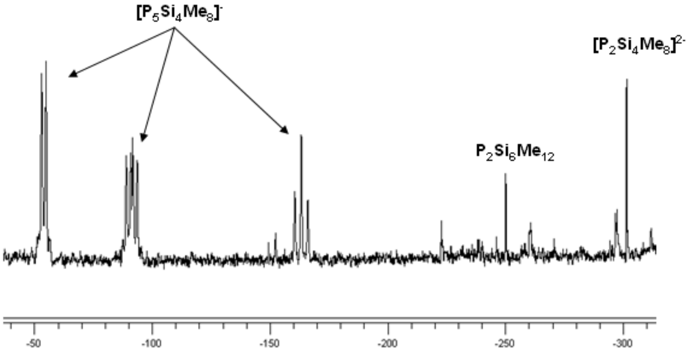


Figure 16: ^{31}P-NMR spectrum from the first reaction mixture.

From the analysis of the ^{31}P-NMR spectrum, the soluble fraction contains a mixture of three main products:

- $[P_2Si_4Me_8]^{2-}$ (δ=-301,3 ppm (s))
- $P_2Si_6Me_{12}$ (δ=-250,0 ppm (s))
- Tentatively identified as $[P_5Si_4Me_8]^-$ (δ=-52,9 ppm (d), δ=-90,8 ppm (m) and δ=-163,2 ppm (t)).

The last cage ($[P_5Si_4Me_8]^-$) is just a possibility, as can be seen in Figure 17. The displayed signals in the ^{31}P-NMR spectrum from the reaction mixture are similar to the ones that are obtained in the spectrum of the simulation. All attempts to isolate $[P_5Si_4Me_8]^-$ failed. Moreover, its formation could not be repeated in further reactions.

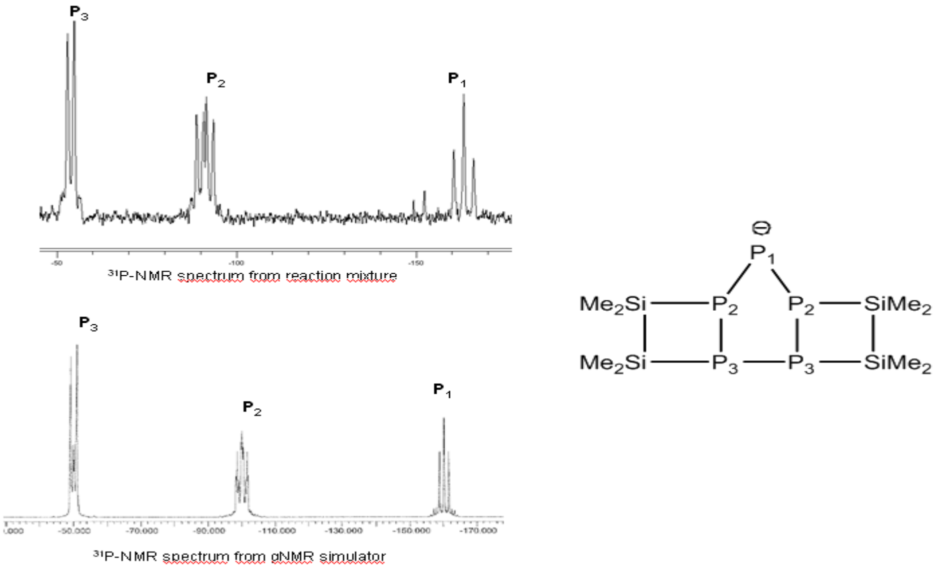


Figure 17: Comparison of the calculated and simulated ^{31}P-NMR spectrum of tentative ($[P_5Si_4Me_8]^-$).

When this reaction was repeated, the result was not reproducible, and a completely different spectrum was obtained (Figure 18).

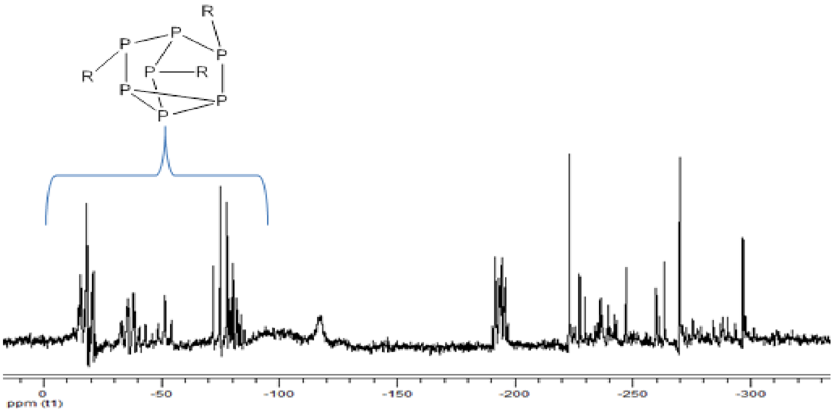
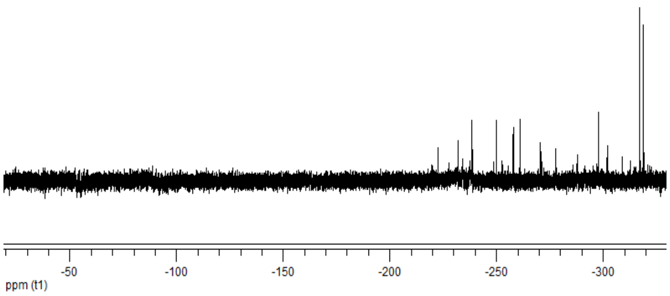
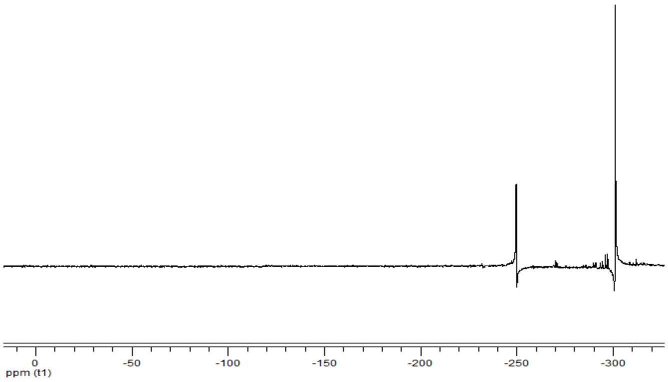
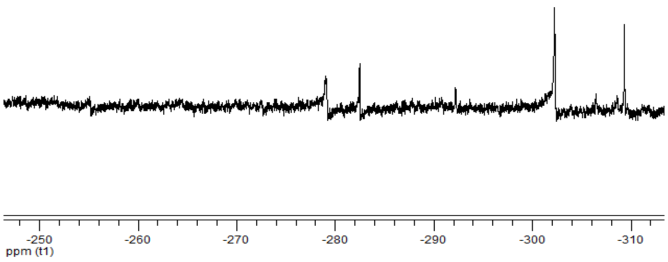


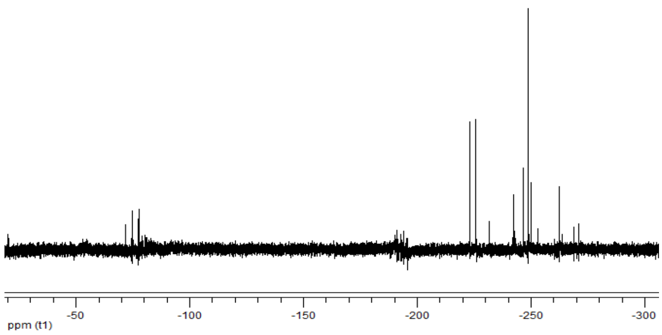
Figure 18: ^{31}P-NMR spectrum from the tentative to reproduce the first reaction.

In this case, the the left part of ^{31}P-NMR spectrum showed a presence of a P_7-system. A typical ^{31}P-NMR spectrum 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"-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.

Many experiments were performed until we finally isolated the $[P_2Si_4Me_8]^{2-}$ ring. All experiments were prepared under the same condition. The only change was the amount of 1,2-dichlorotetramethyldisilane added. In Table 1, a resume of the different experiments is summarised.

Table 1: Summary of attempts to synthesise $[P_2Si_4Me_8]^{2-}$.

Difference on the reaction conditions	***31P-NMR spectra from the reaction mixture***
- 10g of $Cl_2Si_2Me_4$ added over 30 min at -50°C.	
- 10g of $Cl_2Si_2Me_4$ added over 40 min at -50°C.	
- 22g of $Cl_2Si_2Me_4$ added over 30 min at -50°C.	

- 36g of $Cl_2Si_2Me_4$ added over 30 min at -50°C.	

As is shown in Table 1, not just the amount of 1,2-dichlorotetramethyldisilane added leads to different results, also different results are obtained changing the time of dropping the amount of $Cl_2Si_2Me_4$.

Finally the desired ring $[P_2Si_4Me_8]^{2-}$ was obtained by adding 15g (0,5 eq.) of 1,2-dichlorotetramethyldisilane to the suspension of $P(Na/K)_3$ over a period of 30 minutes. The ^{31}P-NMR spectrum of the reaction mixture (Figure 19) displayed just the signal of the dianion.

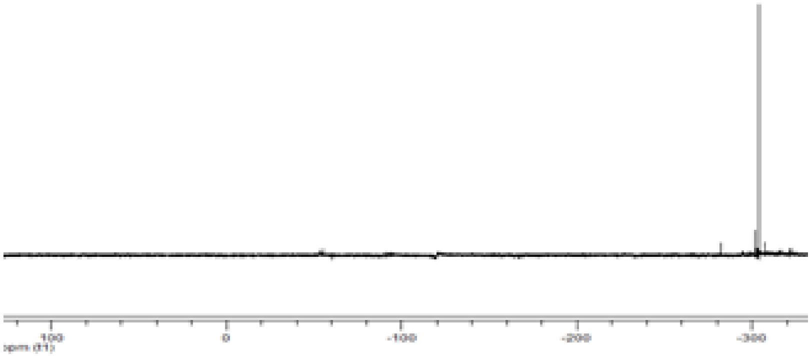


Figure 19: ^{31}P-NMR spectrum from the ring $[P_2Si_4Me_8]^{2-}$.

Crystals could be grown from dimethoxyethane at -30°C. The structure is illustrated in Figure 20.

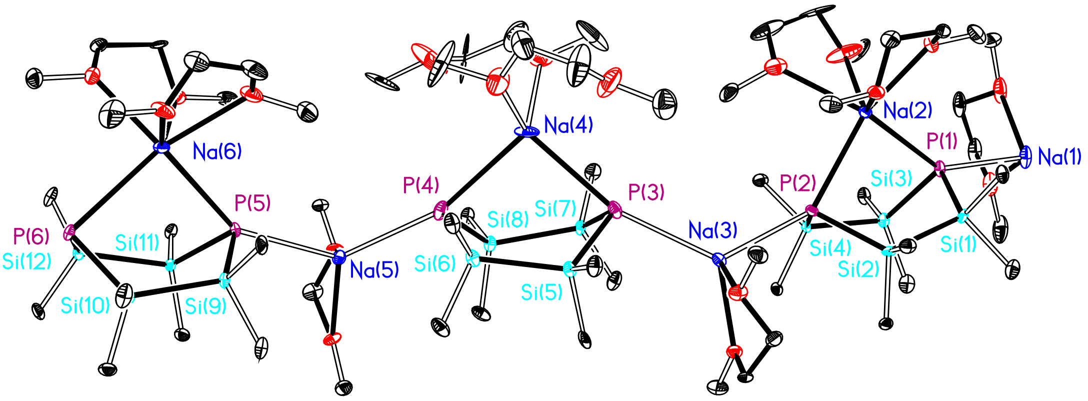


Figure 20: ORTEP plot (50% probabilities, top view of the molecular structure of $[P_2Si_4Me_8]Na_2$.xDME and arrangement in the crystal. Important bond lenghts (Ǻ) and bond angles(°) are: Na(3)-P(3): 2.880(4); Na(4)-P(3): 2.962(5); Na(4)-P(4): 3.022(5); Na(5)-P(4): 2.886(4); Na(4)-O(11): 2.340(9); Na(4)-O(10): 2.345(9); P(3)-Si(5): 2.208(3); P(3)-Si(7): 2.212(3); P(4)-Si(6): 2.205(4); P(4)-Si(8): 2.219(3); Si(5)-C(9): 1.890(8); Si(5)-C(10): 1.891(10); Si(5)-Si(6): 2.364(4); Si(6)-C(12): 1.891(9); Si(6)-C(11): 1.905(9); Si(7)-C(14): 1.882(9); Si(7)-C(13): 1.902(10); Si(7)-Si(8): 2.355(4); Si(8)-C(16): 1.887(9); Si(8)-C(15): 1.925(8).

Table 2: Crystal data and structure refinement for $[P_2Si_4Me_8]^{2-}$.

Empirical formula	$C_{60} H_{162} Na_6 O_{18} P_6 Si_{12}$
Formula weight	1832.74
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, Pna2(1)
Unit cell dimensions	a = 17.988(4) Å alpha = 90 deg. b = 10.982(2) Å beta = 90 deg. c = 54.978(11) Å gamma = 90 deg.
Volume	10861(4) Å^3
Z, Calculated density	4, 1.121 Mg/m^3
Absorption coefficient	0.304 mm^{-1}
F(000)	3960
Crystal size	0.35 x 0.30 x 0.22 mm
Theta range for data collection	1.89 to 26.31 deg.
Limiting indices	-22<=h<=22, -13<=k<=13, -68<=l<=68
Reflections collected / unique	83228 / 21902 [R(int) = 0.1757]
Completeness to theta = 26.31	99.8 %
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21902 / 1 / 962
Goodness-of-fit on F^2	0.984
Final R indices [I>2sigma(I)]	R1 = 0.0863, wR2 = 0.1501
R indices (all data)	R1 = 0.1681, wR2 = 0.1771
Absolute structure parameter	0.59(17)
Largest diff. peak and hole	0.517 and -0.431 e. Å^{-3}

The crystal structure of $[P_2Si_4Me_8]^{2-}$ was also obtained by Dr. Carsten von Hänisch[34] (Figure 21). In his synthesis he uses nBuLi and he does the reaction in three complicated steps[35].

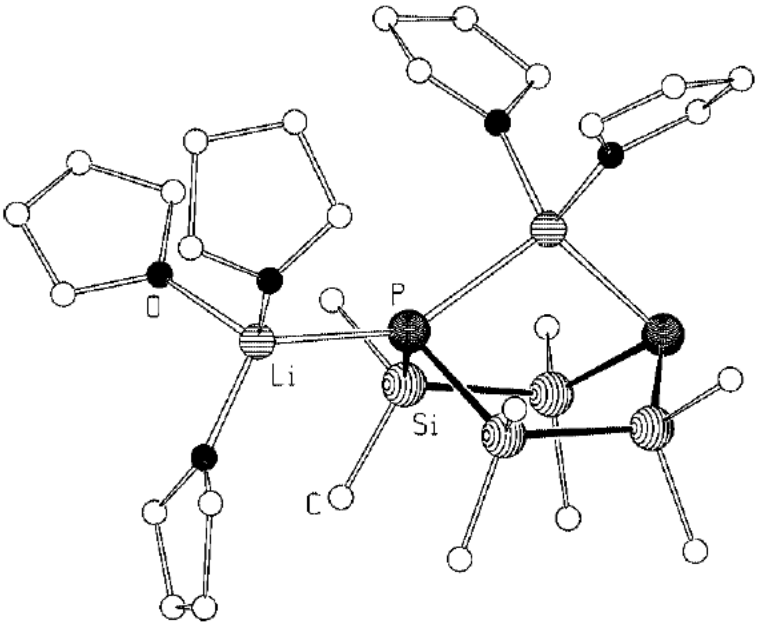


Figure 21: Crystal structure of $[P_2Si_4Me_8]^{2-}$ synthethised by Dr. Carsten von Hänisch.

Comparing the two crystal structures, the most importante difference is that Figure 20 shows a polymeric chain of rings, the sodium ions are always betwen the two P-atoms. In Figure 21 one of the lithium ions is at bridging position between the two phosphorus atoms and further coordinated by two THF ligands and the second Li^+ ion binds to one of the phosphorus atoms only and carries three THF molecules.

The P-Na-P bond angle are similar to the P-Li-P bond angle. Both rings showed boat conformation.

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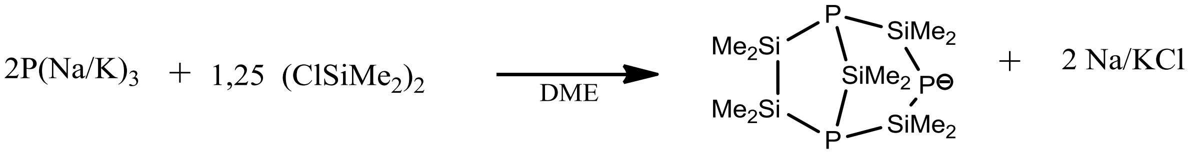
[34] Hänisch. C.; Matern. E.; Z. Anorg. Allg. Chem., **2005**, 631, 1655.

[35] Hänisch. C.; Matern. E.; Z. Anorg. Allg. Chem., **2008**, 634, 23.

3.1.2- Synthesis of [$P_3Si_5Me_{10}$]$^-$

The reaction of P(Na/K)$_3$ with 1,25 equivalent of 1,2-dichlorotetramethyldisilane led to the formation of the cage [$P_3Si_5Me_{10}$]$^-$.



Though the monoanion didn't crystallize from DME and other solvents, the analysis of the ^{31}P-NMR spectra gave no doubt on the identity of the product. The spectrum consists of two single signals at -246,7ppm and -262,6ppm.

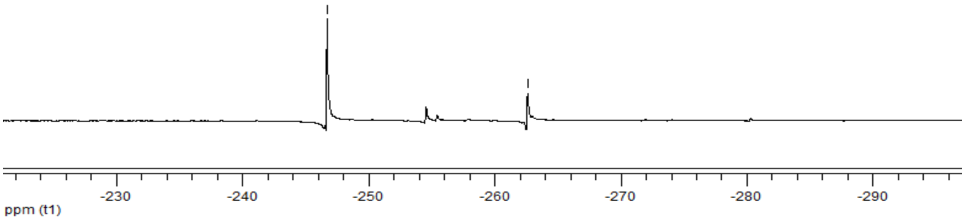


Figure 21: ^{31}P-NMR spectrum of [$P_3Si_5Me_{10}$]$^-$.

This reaction could not be reproduced. Another method for the synthesis of this cage was introduced successfully by Dr. Günter Tekautz during his PhD thesis. In this method, the reaction of $MeSi(SiMe_2Cl)_3$ with 1,25 equivalent of P(Na/K)$_3$ leads to the formation of the cage [$P_3Si_5Me_{10}$]$^-$ [36].

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[36] Tekautz, G.; Baumgartner, J.; Dransfeld, A.; Hassler, K.; Eur. J. Inorg. Chem., **2007**, 4071.

In this method, a solution of tris(chlorodimethylsilyl)methylsilane in DME was added to a suspension of "Na_xP/K_xP",prepared from white phosphorus in DME. Crystals of this anion were obtained also by Dr. Günter Tekautz in DME/hexane solution at -30°C (Figure22)[36].

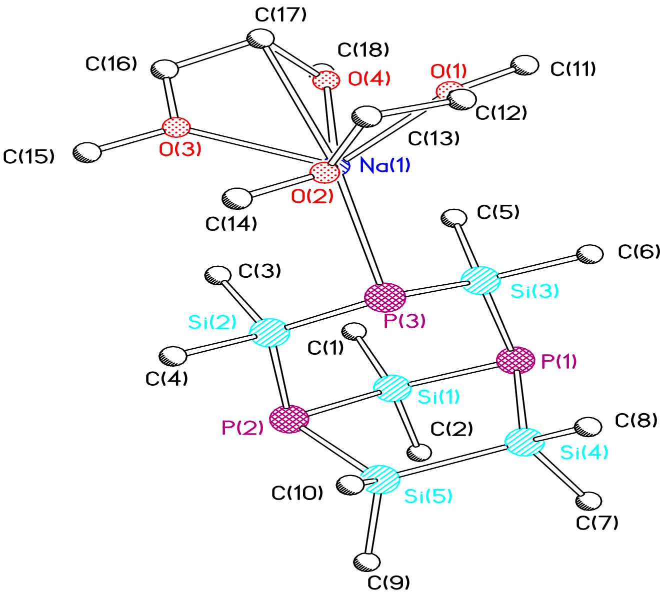

Figure 22: Crystal structure of $[P_3Si_5Me_{10}]^-$.

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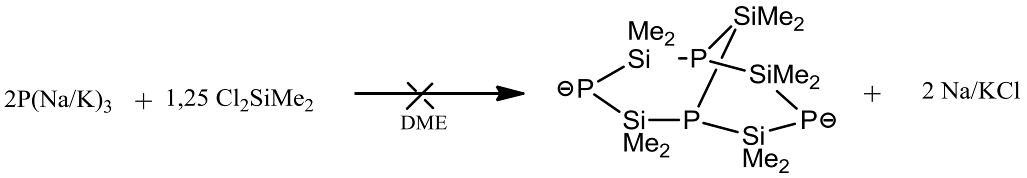
[36] Tekautz, G.; Baumgartner, J.; Dransfeld, A.; Hassler, K.; Eur. J. Inorg. Chem., **2007**, 4071.

3.1.3- *Attempted synthesis of* $[P_4Si_5Me_{10}]^{2-}$ *from* Cl_2SiMe_2

The reaction of P(Na/K)$_3$ with 1,25 equivalent of 1,2-dichlorodimethylsilane did not lead to the formation of the cage $[P_4Si_5Me_{10}]^{2-}$.



Despite several attempts using different reaction conditions (varying temperature and the time of adding the silane) the desired cage could not be synthetized.

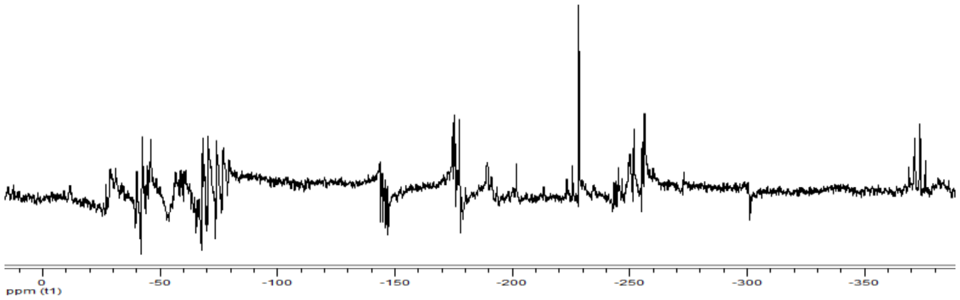


Figure 23: ^{31}P-NMR spectrum of the reaction mixture.

The first ^{31}P-NMR spectrum of the solution displayed a variety of signals, however, none of them correspond to the cage $[P_4Si_5Me_{10}]^{2-}$. We expected that by changing the silane which is added to the P(Na/K)$_3$ solution, different cages could be isolated. By this way it was possible to isolate the cage $Bi_2(SiMe_2)_5$ from the reaction between dichlorodimethylsilane and sodium potassium bismuthide.

$[P_4Si_5Me_{10}]^{2-}Li^{2+}$ has been mentioned in the literature before, but was not further caracterized[37].

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[37] Fritz, G.; Biastoch, R.; Z. Anorg. Allg. Chem., **1986**, 535, 63.

3.1.4- Attempted synthesis of new cages adding Ph_2SiCl_2 and $Cl_2MeSiSi(SiMe_3)_3$ to the $P(Na/K)_3$ suspension

Other attempts to form cages changing the silane added to the $P(Na/K)_3$ suspension were:

$$P(Na/K)_3 \quad + \quad Ph_2SiCl_2 \quad \cancel{\xrightarrow[\text{DME}]{}} \quad ? \quad + \quad 2\ Na/KCl$$

$$2\ P(Na/K)_3 \quad + \quad 3\ Cl_2Si_5Me_{10} \quad \cancel{\xrightarrow[\text{DME}]{}} \quad ? \quad + \quad 2\ Na/KCl$$

In the first case, adding one equivalent of Ph_2SiCl_2 a reddish solution was formed and many signals were observed in the ^{31}P-NMR spectrum. Two signals could match with the cage $[P_2Si_4Ph_8]^{2-}$ and the cage $P_2Si_6Ph_{12}$ at -301,9 ppm and -250,9 ppm respectively.

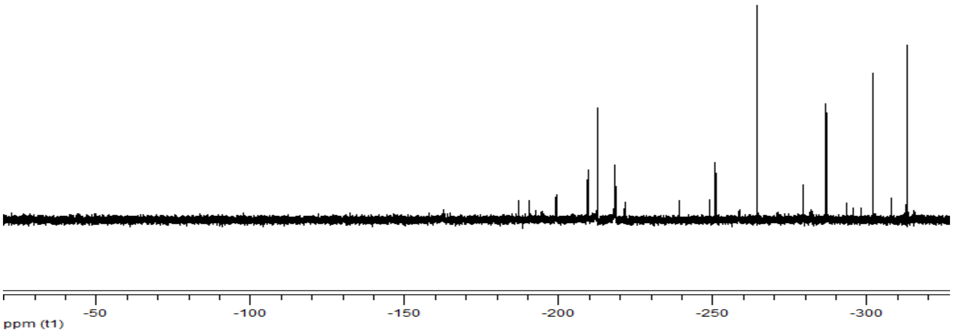


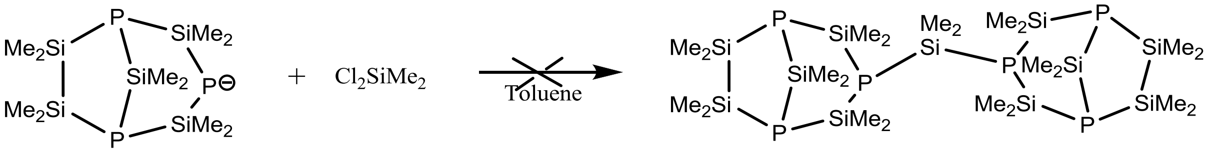
Figure 24: ^{31}P-NMR spectrum of the reaction mixture using Ph_2SiCl_2.

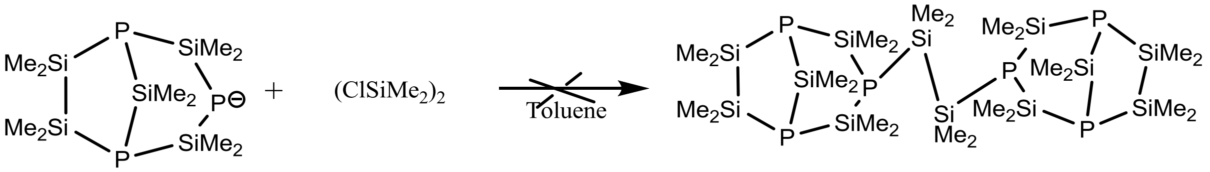
In the second case $Cl_2Si_5Me_{10}$ was added to the solution of $P(Na/K)_3$ in a ratio of 2:3. No signals were detected in the ^{31}P-NMR spectrum from the yellowish solution. Just insoluble polymeric compounds were formed.

3.2- Syntheses of new compounds and new reactions

3.2.1- Reactions of $[P_3Si_5Me_{10}]^-$

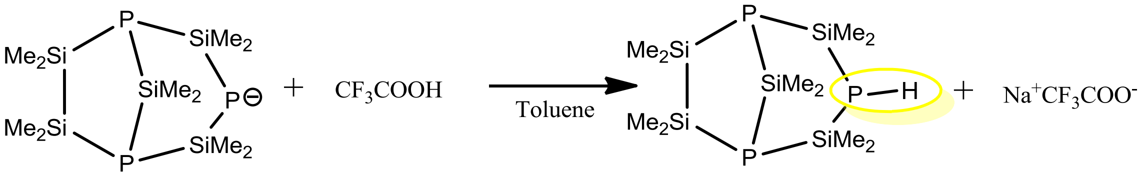
3.2.1.1- Attempts to bridge $[P_3Si_5Me_{10}]^-$





The reactions of $[P_3Si_5Me_{10}]^-$ with Cl_2SiMe_2 and $(ClSiMe_2)_2$ in a molar ratio of 1:1 was expected to give the cages $P_6Si_{11}Me_{22}$ and $P_6Si_{12}Me_{24}$ respectively, which consist of two $[P_3Si_5Me_{10}]^-$ cages connected by one or two $SiMe_2$ groups. In both reactions the silane was added dropwise to a solution of the anion at low temperature. According to the ^{31}P- NMR and ^{29}Si-NMR spectra a mixture of compounds was obtained. Attempts to separate the mixtures by fractional crystallization failed.

3.2.1.2- Protonation of $[P_3Si_5Me_{10}]^-$



Trifluoroacetic acid was used in this attempt to protonate the anion $[P_3Si_5Me_{10}]^-$.

The acid was added to a toluene solution of the anion at -50°C. A colourless solution was formed and the cage $P_3Si_5Me_{10}H$ was characterized from ^{31}P-NMR and ^{29}Si-NMR spectra. The structure could be confirmed by x-ray analysis as crystals could be grown from heptane at -30°C.

From the ^{31}P-NMR spectrum we could observe that the cage exists in two conformations. The hydrogen atom can be in the axial and equatorial position as shown in Figure 25.

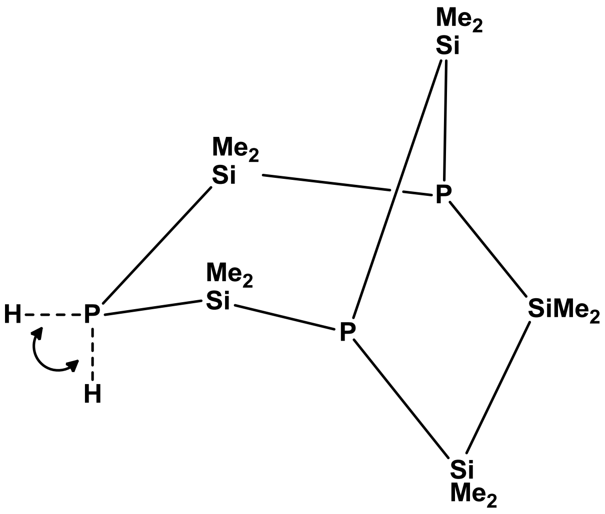


Figure 25: Two possible conformations of the cage $[P_3Si_5Me_{10}]^-$.

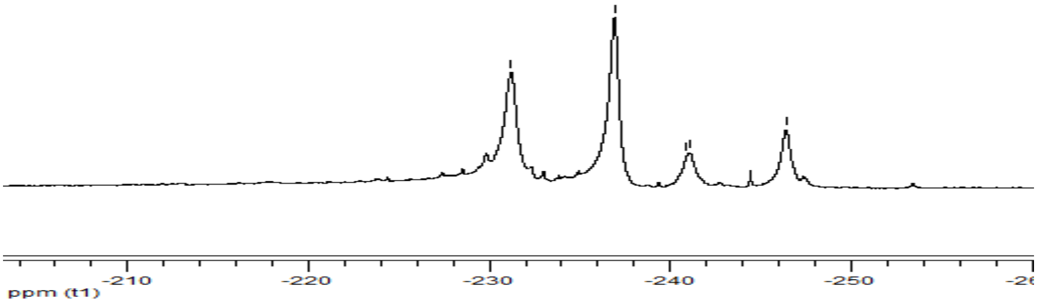


Figure 26: Proton decoupled ^{31}P-NMR spectrum of the $P_3Si_5Me_{10}H$ solution.

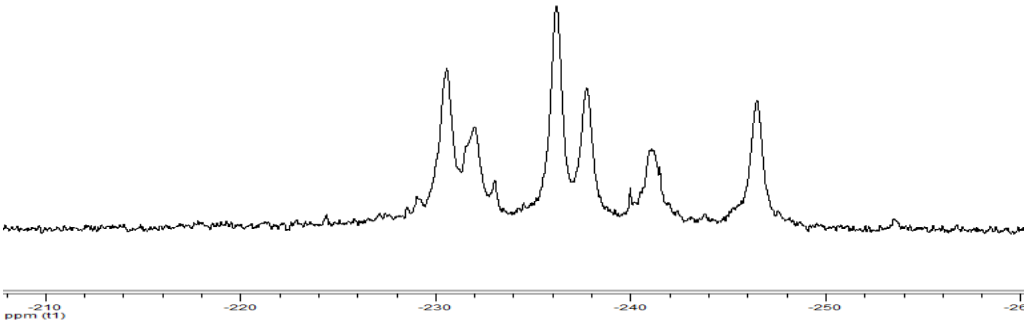


Figure 27: Proton coupled ^{31}P-NMR spectrum of $P_3Si_5Me_{10}H$ in solution.

As we see in the spectrums above, the signals at -231,1 ppm and at -236,9 ppm are singlets in the decoupled spectrum and they split in to doublets in the coupled spectrum. This confirms the two possible conformations of the cage.

In the crystal structure obtained the hydrogen was located in the axial position.

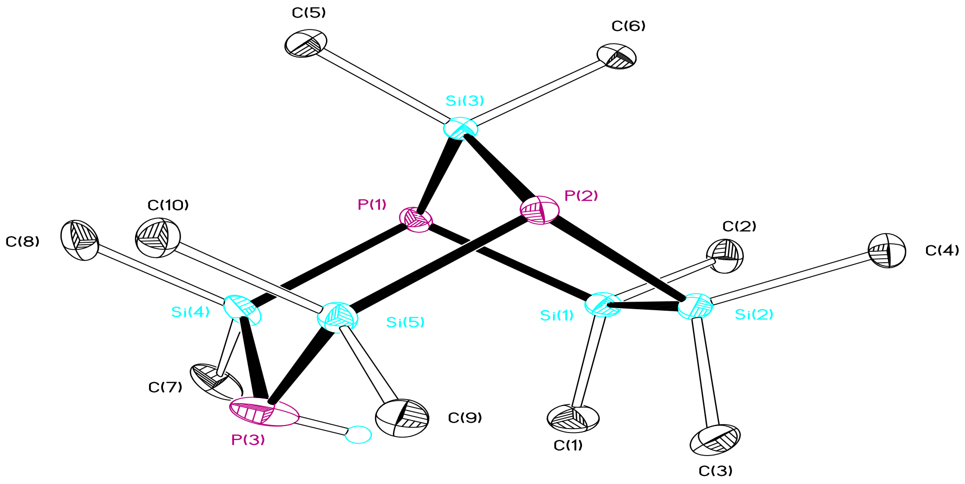


Figure 28: ORTEP plot (50% probabilities, top view° of the molecular structure of $P_3Si_5Me_{10}H$. Important bond lenghts (Å) and bond angles(°) are: P(1)-Si(4): 2.2535(10); P(1)-Si(3): 2.2625(9); P(1)-Si(1): 2.2693(9); P(2)-Si(5): 2.2436(10); P(2)-Si(3): 2.2540(9); P(2)-Si(2): 2.2645(9); P(3)-Si(5): 2.2462(10); P(3)-Si(4): 2.2485(10); Si(1)-C(2): 1.877(2); Si(1)-C(1): 1.880(3); Si(1)-Si(2): 2.3687(9); Si(2)-C(3): 1.874(2); Si(2)-C(4): 1.882(2); Si(3)-C(5): 1.870(2); Si(3)-C(6): 1.875(2); Si(4)-C(8): 1.875(3); Si(4)-C(7): 1.877(3); Si(5)-C(9): 1.874(2); Si(5)-C(10): 1.874(2); Si(4)-P(1)-Si(3): 103.86(3); Si(4)-P(1)-Si(1): 104.64(3); Si(3)-P(1)-Si(1): 94.50(3); Si(5)-P(2)-Si(3): 104.48(3); Si(5)-P(2)-Si(2): 103.84(3); Si(3)-P(2)-Si(2): 94.41(3); Si(5)-P(3)-Si(4): 106.06(4); C(2)-Si(1)-C(1): 106.24(13); C(2)-Si(1)-P(1): 108.16(9); C(1)-Si(1)-P(1): 112.55(9); C(2)-Si(1)-Si(2): 110.47(8); C(1)-Si(1)-Si(2): 111.13(9); P(1)-Si(1)-Si(2): 108.24(3); C(3)-Si(2)-C(4): 106.74(12); C(3)-Si(2)-P(2): 112.82(8); C(4)-Si(2)-P(2): 107.26(8); C(3)-Si(2)-Si(1): 109.68(9); C(4)-Si(2)-Si(1): 111.74(8); P(2)-Si(2)-Si(1): 108.62(3); C(5)-Si(3)-C(6): 107.21(11); C(5)-Si(3)-P(2): 111.96(9); C(6)-Si(3)-P(2): 104.35(8); C(5)-Si(3)-P(1): 111.63(9); C(6)-Si(3)-P(1): 106.30(8); P(2)-Si(3)-P(1): 114.67(3); C(8)-Si(4)-C(7): 107.58(14); C(8)-Si(4)-P(3): 108.52(9); C(7)-Si(4)-P(3): 105.44(10); C(8)-Si(4)-P(1): 109.48(9); C(7)-Si(4)-P(1): 107.72(9); P(3)-Si(4)-P(1): 117.63(4); C(9)-Si(5)-C(10): 107.67(11); C(9)-Si(5)-P(2): 106.52(8); C(10)-Si(5)-P(2): 108.84(9); C(9)-Si(5)-P(3): 105.62(9); C(10)-Si(5)-P(3): 109.21(9); P(2)-Si(5)-P(3): 118.46(4).

The Si-P bond of the P^- atom in the anion $[P_3Si_5Me_{10}]^-$ is shorter than the P-Si bond of the P-H atom in $P_3Si_5Me_{10}H$ by about 0,059Å ($Si_{(5)}P_{(3)}$).
The $Si_{(5)}P_{(2)}$ bond of the anion is longer than the one of $P_3Si_5Me_{10}H$ by about 0,040Å. With 2.369 Å the Si-Si bond length of $P_3Si_5Me_{10}H$ is within the range found in $[P_3Si_5Me_{10}]^-$.[39]

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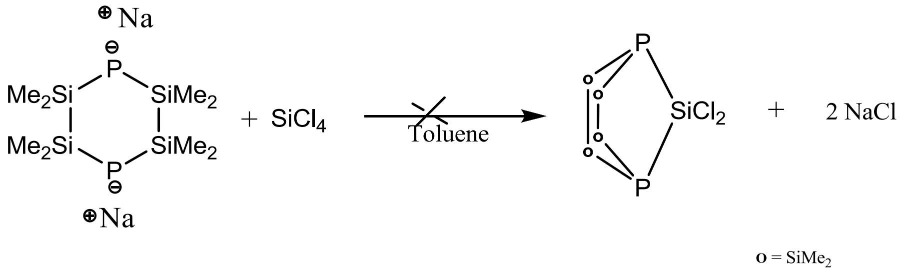
[39] Tekautz, G.; Baumgartner, J.; Dransfeld, A.; Hassler, K.; Eur. J. Inorg. Chem., **2007**, 4073.

Table 3: Crystal data and structure refinement for $P_3Si_5Me_{10}H$.

Empirical formula	C_{10} H_{31} P_3 Si_5
Formula weight	384.71
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	rhombohedric, R-3
Unit cell dimensions	a = 36.516(5) Å alpha = 90 deg. b = 36.516(5) Å beta = 90 deg. c = 9.1618(18) Å gamma = 120 deg.
Volume	10580(3) $Å^3$
Z, Calculated density	18, 1.087 Mg/m^3
Absorption coefficient	0.496 mm^{-1}
F(000)	3708
Crystal size	0.46 x 0.32 x 0.24 mm
Theta range for data collection	1.93 to 26.38 deg.
Limiting indices	-45<=h<=45, -45<=k<=45, -11<=l<=11
Reflections collected / unique	28343 / 4818 [R(int) = 0.0581]
Completeness to theta = 26.38	99.8 %
Absorption correction	SADABS
Max. and min. transmission	0.8903 and 0.8040
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4818 / 0 / 177
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.0971
R indices (all data)	R1 = 0.0577, wR2 = 0.1024
Largest diff. peak and hole	0.522 and -0.471 e. $Å^{-3}$

3.2.2- Derivatization of $[P_2Si_4Me_8]^{2-}$

3.2.2.1- Reaction of $[P_2Si_4Me_8]^{2-}$ with $SiCl_4$



The cage $P_2(SiMe_2)_4SiCl_2$ was the desired product of these reactions. $SiCl_4$ was added to a solution of the dianion $[P_2Si_4Me_8]^{2-}$ at low temperature. As shown in Figure 29, the ^{31}P-NMR spectrum of the orange solution displayed only one signal at -206,3 ppm.

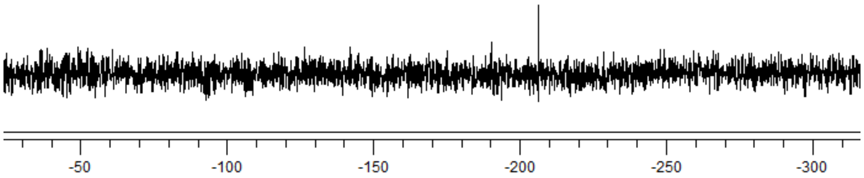


Figure 29: ^{31}P-NMR spectrum of the reaction mixture.

The ^{29}Si-NMR displayed two signals, at 15,4 ppm and 25,1 ppm(Figure 30). As there is no splitting due to SiP coupling, the presence of the cage can be ruled out.

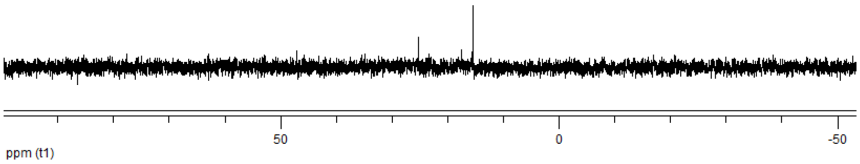
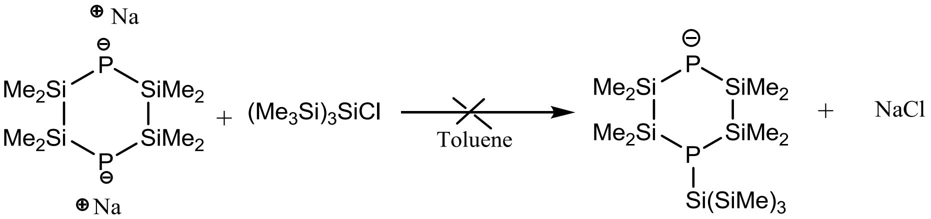


Figure30: ^{29}Si-NMR spectrum of the reaction mixture.

3.2.2.2- *Reaction of [$P_2Si_4Me_8$]$^{2-}$ with (Me_3Si)$_3$SiCl*

The target product of this reaction was the anion [$P_2Si_8Me_{11}$]$^-$.



The reaction of the dianion with (Me_3Si)$_3$SiCl was carried out at low temperature in a ratio of 1:1. A toluene/DME solution was added dropwise to the DME solution of the dianion. The ^{31}P-NMR from the yellow solution displayed many signals (Figure 31). A mixture of compounds had formed.

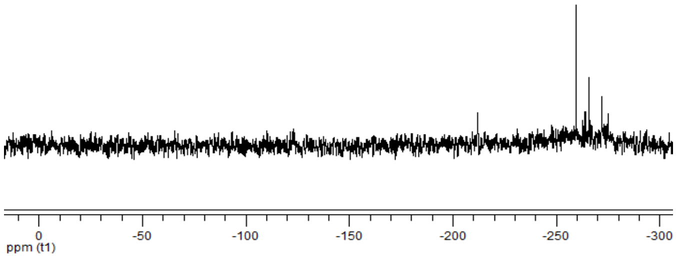
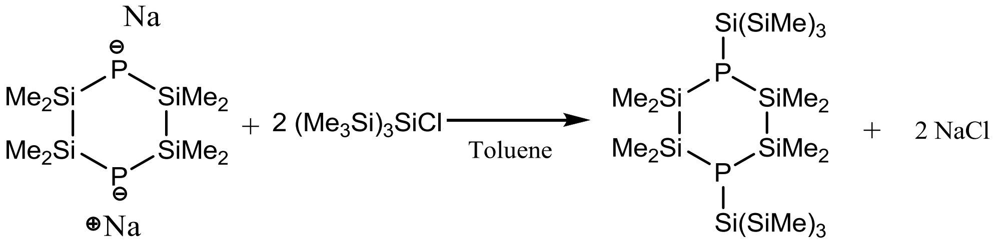


Figure 31: ^{31}P-NMR spectrum of the reaction mixture.

The signals displayed in the ^{31}P-NMR at -259,4 ppm and -314,0 ppm are good candidates to represent the target product.

The reaction of the dianion with $(Me_3Si)_3SiCl$ was repeted at low temperature with a ratio of 1:2.



A toluene/DME solution was added dropwise to the DME solution of the dianion. The reaction lead to the formation of $P_2Si_{12}Me_{14}$ consisting of two hypersilyl groups attached to the two P atoms of the dianion $[P_2Si_4Me_8]^{2-}$. The ^{31}P-NMR from the colorless solution displayed a single signal at -269,5 ppm. The ^{29}Si-NMR spectrum displayed a singlet at 0,7 ppm from the $(SiMe)_3$ groups, a pseudotriplet at -14,6 ppm from the $SiMe_2$ groups and a doublet at -83,5 ppm from the hypersilyl Si-atom.

Crystals suitable for x-ray experiments were formed from the solution in heptane (Figure 32).

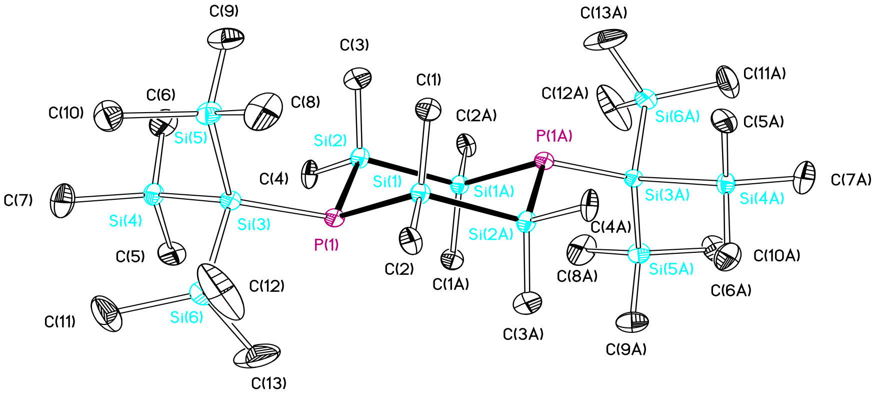


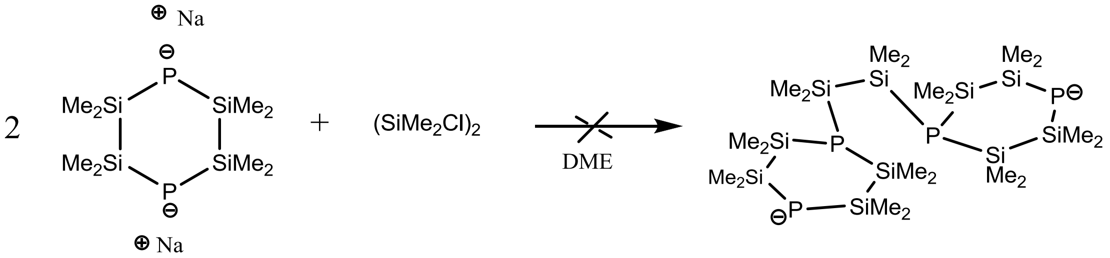
Figure 32: ORTEP plot (50% probabilities, top view° of the molecular structure of $P_2Si_{12}Me_{14}$. Important bond lenghts (Å) and bond angles(°) are: P(1)-Si(1): 2.232(3); P(1)-Si(2): 2.242(3); P(1)-Si(3): 2.282(3); Si(1)-C(2): 1.857(8); Si(1)-C(1): 1.873(9); Si(1)-Si(2): 2.334(3); Si(2)-C(4): 1.859(9); Si(2)-C(3): 1.874(9); Si(2)-Si(1): 2.334(3); Si(3)-Si(5): 2.344(3); Si(3)-Si(6): 2.354(4); Si(3)-Si(4): 2.355(3); Si(4)-C(7): 1.827(10); Si(4)-C(6): 1.848(10); Si(4)-C(5): 1.849(9); Si(5)-C(9): 1.850(11); Si(5)-C(10): 1.866(11); Si(5)-C(8): 1.874(11); Si(6)-C(11): 1.827(11); Si(6)-C(13): 1.845(12); Si(6)-C(12): 1.868(11); Si(1)-P(1)-Si(2): 98.59(12); Si(1)-P(1)-Si(3): 108.12(12); Si(2)-P(1)-Si(3): 116.01(13); C(2)-Si(1)-C(1): 108.1(4); C(2)-Si(1)-P(1): 107.4(3); C(1)-Si(1)-P(1): 116.8(3); C(2)-Si(1)-Si(2): 104.5(3); C(1)-Si(1)-Si(2): 106.6(3); P(1)-Si(1)-Si(2): 112.71(13); C(4)-Si(2)-C(3): 109.5(5); C(4)-Si(2)-P(1): 110.1(3); C(3)-Si(2)-P(1): 117.1(3); C(4)-Si(2)-Si(1): 101.0(3); C(3)-Si(2)-Si(1): 110.8(3); P(1)-Si(2)-Si(1): 107.10(13); P(1)-Si(3)-Si(5): 122.17(13); P(1)-Si(3)-Si(6): 104.97(12); Si(5)-Si(3)-Si(6): 108.48(13); P(1)-Si(3)-Si(4): 106.26(12); Si(5)-Si(3)-Si(4): 107.23(13); Si(6)-Si(3)-Si(4): 106.88(13); C(7)-Si(4)-C(6): 105.6(5); C(7)-Si(4)-C(5): 106.1(5); C(6)-Si(4)-C(5): 112.7(5); C(7)-Si(4)-Si(3): 114.9(4); C(6)-Si(4)-Si(3): 108.7(3); C(5)-Si(4)-Si(3): 108.9(3); C(9)-Si(5)-C(10): 107.6(6); C(9)-Si(5)-C(8): 107.0(6); C(10)-Si(5)-C(8): 107.4(6); C(9)-Si(5)-Si(3): 114.6(4); C(10)-Si(5)-Si(3): 105.9(4); C(8)-Si(5)-Si(3): 113.9(4); C(11)-Si(6)-C(13): 109.5(7); C(11)-Si(6)-C(12): 104.7(6); C(13)-Si(6)-C(12): 107.4(8); C(11)-Si(6)-Si(3): 112.1(4); C(13)-Si(6)-Si(3): 109.4(4); C(12)-Si(6)-Si(3): 113.6(5).

All Si-P bonds of this ring are longer than the ones of the dianion $[P_2Si_4Me_8]^{2-}$, Si-Si bonds are similar. The conformation also changes, as the PSi_4P ring adopts the chair conformation.

Table 4: Crystal data and structure refinement for $P_2Si_{12}Me_{14}$.

Empirical formula	$C_{26} H_{78} P_2 Si_{12}$
Formula weight	789.90
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P1
Unit cell dimensions	a = 8.9590(18) Å alpha = 98.43(3) deg. b = 9.6805(19) Å beta = 97.14(3) deg. c = 16.370(3) Å gamma = 116.41(3) deg.
Volume	1228.7(4) $Å^3$
Z, Calculated density	1, 1.068 Mg/m^3
Absorption coefficient	0.398 mm^{-1}
F(000)	432
Crystal size	0.44 x 0.28 x 0.15 mm
Theta range for data collection	2.41 to 22.50 deg.
Limiting indices	-9<=h<=9, -10<=k<=10, -17<=l<=17
Reflections collected / unique	7169 / 3217 [R(int) = 0.0758]
Completeness to theta = 22.50	99.7 %
Absorption correction	SADABS
Max. and min. transmission	0.9427 and 0.8444
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3217 / 0 / 194
Goodness-of-fit on F^2	1.199
Final R indices [I>2sigma(I)]	R1 = 0.1053, wR2 = 0.2394
R indices (all data)	R1 = 0.1261, wR2 = 0.2504
Largest diff. peak and hole	0.855 and -0.568 e. $Å^{-3}$

3.2.2.3- Reaction of $[P_2Si_4Me_8]^{2-}$ with $(SiMe_2Cl)_2$



The reaction of $[P_2Si_4Me_8]^{2-}$ with $Cl_2Si_2Me_4$ in a molar ratio of 2:1 was expected to lead to the dianion $[P_4Si_{10}Me_{20}]^{2-}$, which consist of two $[P_2Si_4Me_8]^{2-}$ cages connected by two $SiMe_2$ groups. The silane was added dropwise to a solution of the dianion at low temperature. The ^{31}P- NMR spectrum from the reaction mixture (Figure 33) showed once more a mixture of compounds and the target product could not be correctly identified. The cage $P_2Si_6Me_{12}$ was present in the solution and crystals from this cage could be grown from DME. This cage was already identified by Dr. Günter Tekautz in his PhD thesis.

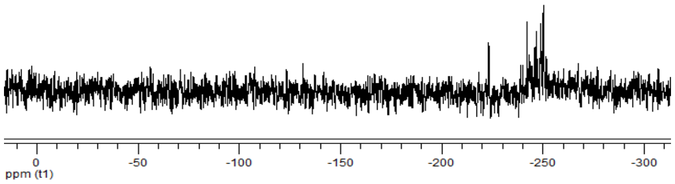
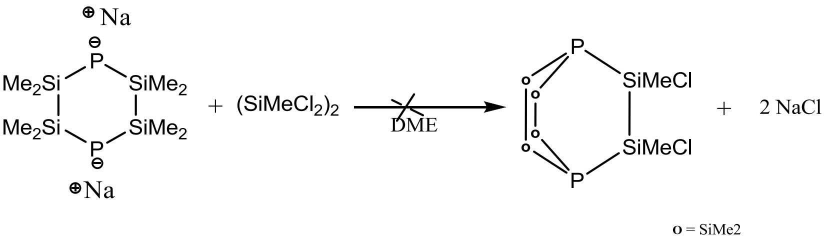


Figure 33: ^{31}P-NMR spectrum of the reaction mixture.

3.2.2.4- Reaction of $[P_2Si_4Me_8]^{2-}$ with $(Cl_2MeSi)_2$



To synthetize the cage $P_2(SiMe_2)_4(SiMeCl)_2$ consisting of two SiMeCl groups bridging the two P-atoms, $(Cl_2MeSi)_2$ was added at -50°C to the solution of $[P_2Si_4Me_8]^{2-}$. The ^{31}P-NMR of the reaction mixture (Figure 34) displayed a very intense signal at -243,3 ppm which could match with the target product, and a smooth signal at -213,9 ppm which might be another Si-P cage.

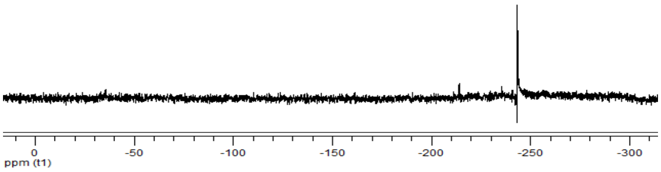


Figure 34: ^{31}P-NMR spectrum of the reaction mixture.

Looking just to the ^{31}P-NMR spectrum one can assume immediately that the desired cage was obtained almost pure. However, in the ^{29}Si-NMR spectrum, quite a lot of impurities are present. Signals are displayed at 27,8 ppm, -3,5 ppm, -11,2 ppm, -18,8 ppm and -21,2 ppm.

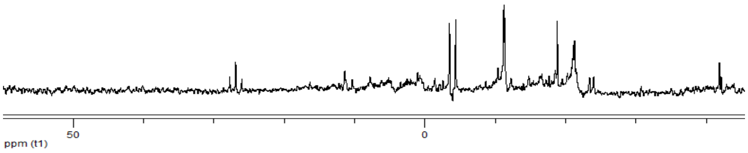
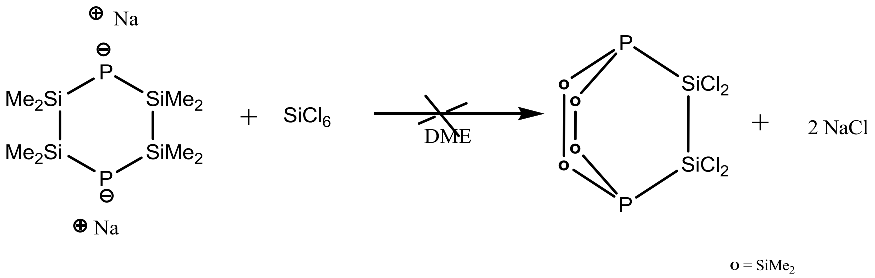


Figure 35: ^{29}Si-NMR spectrum of the reaction mixture.

The doublet at -21,2 ppm and the triplet at 26,8 ppm could match with the bycycloheptane cage $P_2(SiMe_2)_4SiMeCl$, which are from $SiMe_2$ groups and the SiMeCl group respectively. No crystals could be obtained.

3.2.2.5- Reactions of $[P_2Si_4Me_8]^{2-}$ with Si_2Cl_6.



The reaction of $[P_2Si_4Me_8]^{2-}$ with Si_2Cl_6 in DME/toluene at -50°C in a molar ratio of 1:1 was expected to lead to the formation of the cage $P_2Si_6Me_4Cl_4$. The ^{31}P-NMR spectrum from the solution displayed two singlets, one with strong intensity at -168,9 ppm and the second one with low intensity at – 109,7 ppm (Figure 36).

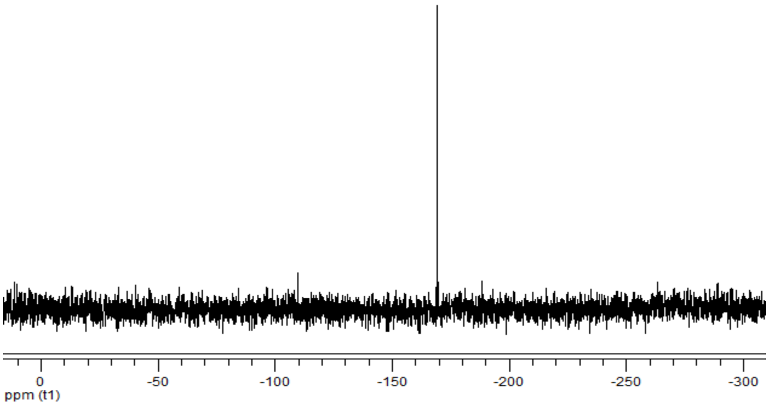
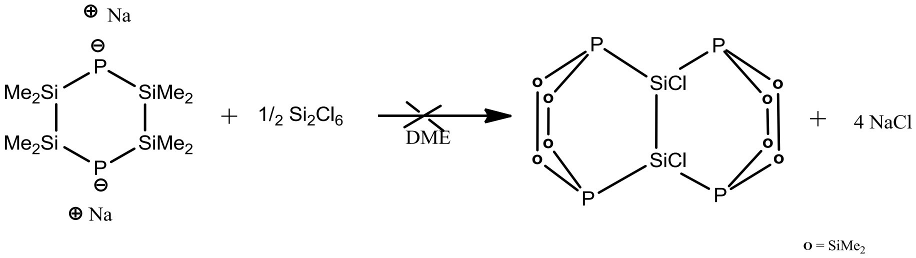


Figure 36: ^{31}P-NMR spectrum of the reaction mixture.

The desired cage could not be obtained pure, but one can clearly see from the spectrum above that there is a major product. In the ^{29}Si-NMR spectrum, just two singlets at 29,6 ppm and 16,4 ppm and a doublet at 19,2 ppm were observed.

By changing the molar ratio to 2:1, the formation f the cage $P_4Si_{10}Me_8Cl_2$ can be expected, which consist in two $[P_2Si_4Me_8]^{2-}$ cages connected to the two SiCl groups.



The ^{31}P-NMR spectrum shows again only a singlet at -168,9 ppm (Figure 37). The ^{29}Si-NMR spectrum displayed 3 signals at 25,8 ppm, 18,9 ppm and 16,1 ppm. As crystals were not obtained from the solutions in both reactions, the target cages could not be correctly identified.

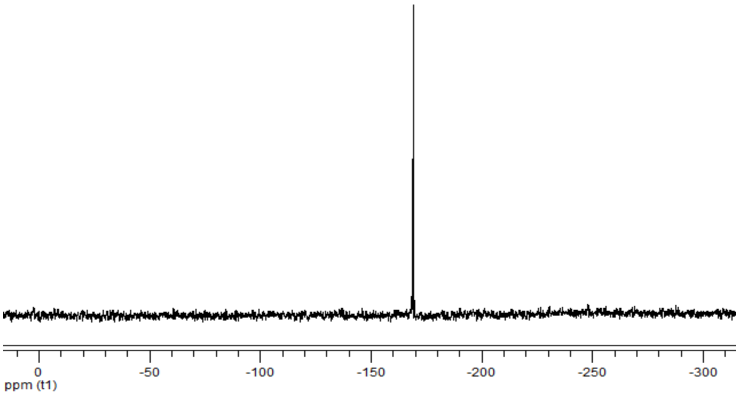
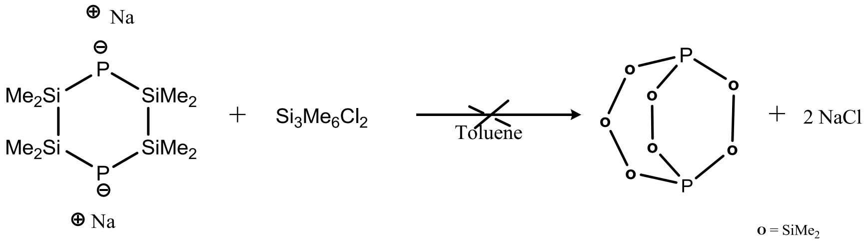


Figure 37: ^{31}P-NMR spectrum of the reaction mixture.

In the ^{29}Si-NMR spectrum, the signals of $SiMe_2$ are missing (approximately between -10 ppm and -20 ppm) so the signal displayed at -168,9 ppm in the ^{31}P-NMR spectrum cannot be from the desired cages.

3.2.2.6- *Reactions of $[P_2Si_4Me_8]^{2-}$ with $Cl_2Si_3Me_6$*



In this reaction the dianion was added dropwise to a solution of $Cl_2Si_3Me_6$ at low temperature. The target product was the cage $P_2Si_7Me_{14}$ which is a bicyclononane.
In Figure 38, the ^{31}P-NMR spectrum of the orange solution is shown, displaying only one signal at -256,3 ppm which might match with the target compound.

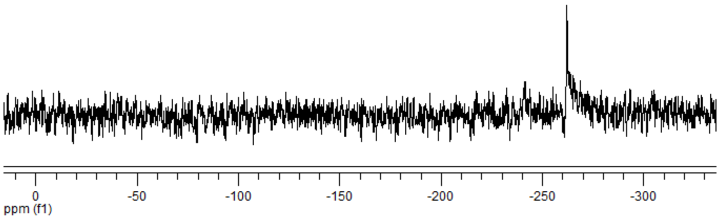
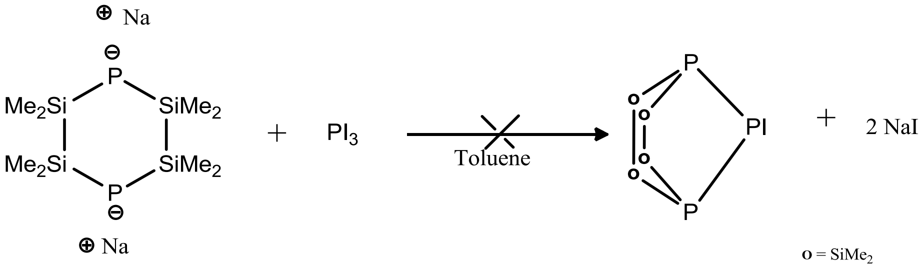


Figure 38: ^{31}P-NMR spectrum of the reaction mixture.

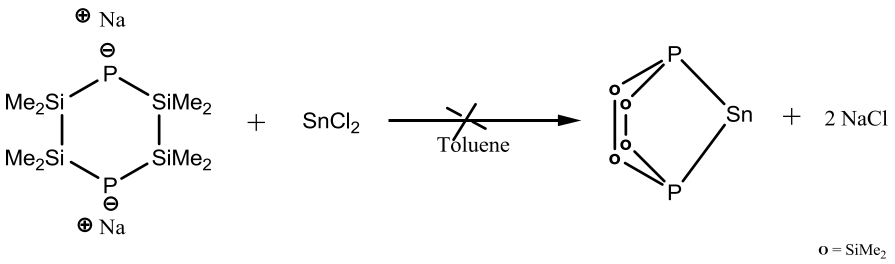
In the ^{29}Si-NMR spectrum, three singlets at -21,4 ppm , -16,9 ppm and -12,0 ppm and one doublet at -19,1 ppm were observed. These signals don't match with the target compound for which three different signals are expected. A doublet for the two $SiMe_2$-groups in the Si_3-bridge which are bonded to the P-atoms, and a triplet at about -30 ppm for the central $SiMe_2$-group with a coupling constant of about 5 to 10 Hz.

3.2.2.7- Reactions of $[P_2Si_4Me_8]^{2-}$ with PI_3



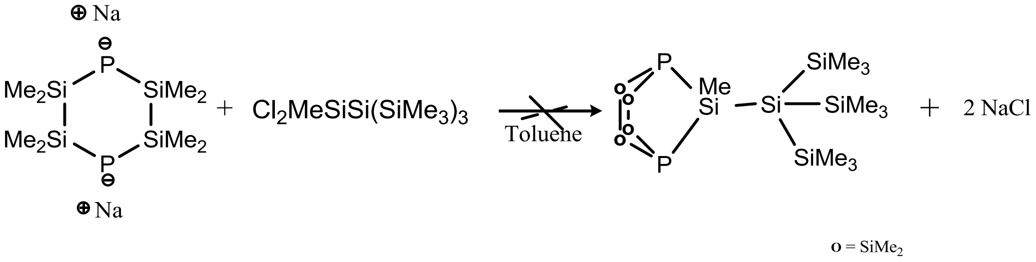
Two ways were tried to synthesize the cage $P_3Si_4Me_8I$, as shown above. First PI_3 was added to the dianion in DME at low temperature in a ratio of 1:1. $[P_2Si_4Me_8]^{2-}$ was destroyed and no signals were displayed in the ^{31}P-NMR spectrum. The second method was adding the dianion $[P_2Si_4Me_8]^{2-}$ in a solution of DME/toluene to a solution of PI_3 in toluene in a molar ratio of 1:1. This time many signals were displayed in the ^{31}P-NMR spectrum, between them one at -250,0 ppm from the cage $P_2Si_6Me_{12}$. Further signals could not be assigned.

3.2.2.8- *Reactions of $[P_2Si_4Me_8]^{2-}$ with $SnCl_2$*



In this attempt, the target product was the cage $P_3Si_4Me_8Sn$ which consist of a tin atom connected to two P-atoms. Tin dichloride was added to a DME/toluene solution of $[P_2Si_4Me_8]^{2-}$ at low temperature. According to the ^{31}P-NMR spectrum, the reaction leads to the complete destruction of the cage.

3.2.2.9- Reactions of $[P_2Si_4Me_8]^{2-}$ with $Cl_2MeSiSi(SiMe_3)_3$



$Cl_2MeSiSi(SiMe_3)_3$ was used in this reaction to obtain the target product $P_2(SiMe_2)_2SiMeSi(Me_3)_3$. $[P_2Si_4Me_8]^{2-}$ dissolved in DME/toluene was added to a toluene solution of $Cl_2MeSiSi(SiMe_3)_3$ at low temperature. The ^{31}P-NMR spectrum from the orange solution displayed signals at -207,3 ppm, -213,0 ppm, -231,9 ppm and -257,3 ppm (Figure 39). This cage should give just a single signal in the ^{31}P-NMR spectrum. As no crystals could be obtained, neither from DME, toluene and hexane, none of this could be assigned.

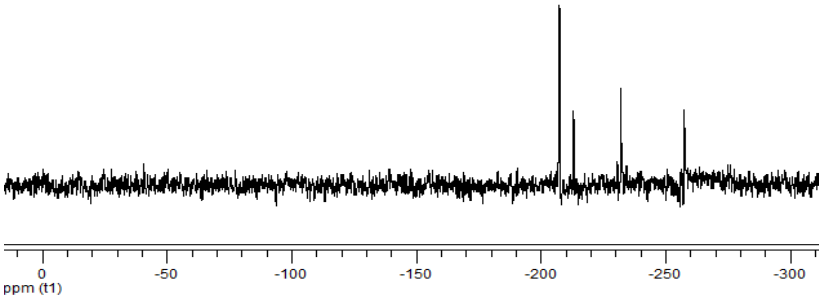
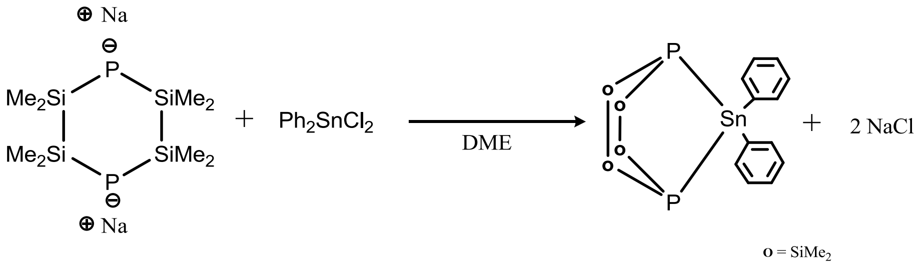


Figure 39: ^{31}P-NMR spectrum of the reaction mixture.

3.2.2.10- Reaction of $[P_2Si_4Me_8]^{2-}$ with Ph_2SnCl_2



The reaction of $[P_2Si_4Me_8]^{2-}$ with Ph_2SnCl_2 in a molar ratio 1:1 gave the cage $P_2Si_4Me_8SnPh_2$, which consist of a $SnPh_2$-group connected to the two P-atoms. $[P_2Si_4Me_8]^{2-}$ was added to Ph_2SnCl_2 at low temperature. The ^{31}P-NMR spectrum from the yellow solution displayed a signal at -232,5 ppm (Figure 40). The ^{29}Si-NMR spectrum displayed a doublet for the $SiMe_2$ groups at -24,6 ppm, besides other signals at -0,9 ppm, -2,0 ppm, -11,1 ppm, which are from impurities with Si-Si bonds. Crystals were obtained from DME solution and the cage could be identified (Figure 40).

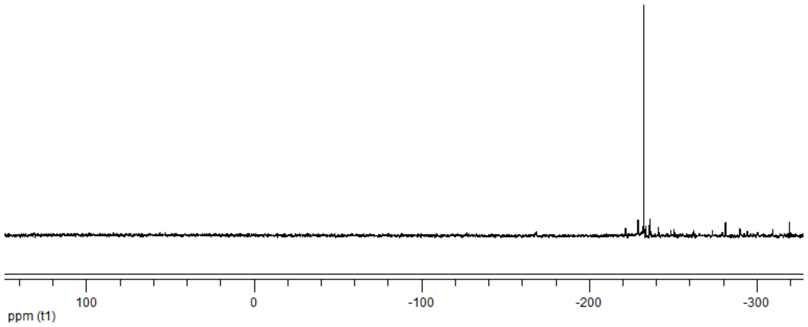


Figure 40: ^{31}P-NMR spectrum of the reaction mixture.

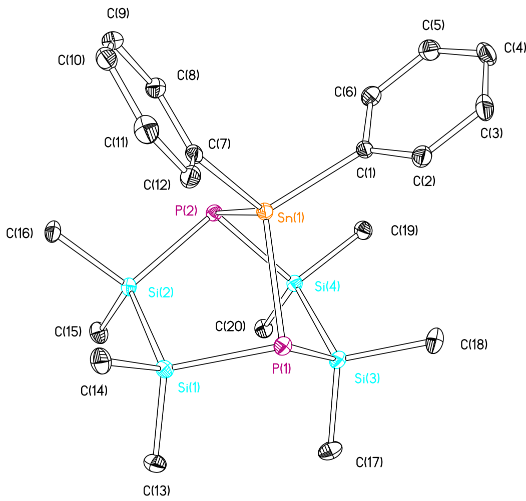


Figure 41: ORTEP plot (50% probabilities, top view° of the molecular structure of $P_2Si_4Me_8SnPh_2$. Important bond lengths (Å) and bond angles(°) are: P(1)-Si(3): 2.2610(13); P(1)-Si(1): 2.2673(10); P(1)-Sn(1): 2.5140(11); P(2)-Si(2): 2.2681(11); P(2)-Si(4): 2.2688(11); P(2)-Sn(1): 2.5111(9); Sn(1)-C(7): 2.142(2); Sn(1)-C(1): 2.147(2); Si(1)-C(14): 1.876(3); Si(1)-C(13): 1.879(3); Si(1)-Si(2): 2.3639(13); Si(2)-C(16): 1.870(3); Si(2)-C(15): 1.873(3); Si(3)-C(17): 1.882(3); Si(3)-C(18): 1.885(3); Si(3)-Si(4): 2.3646(13); Si(4)-C(19): 1.878(3); Si(4)-C(20): 1.881(2); C(1)-C(2): 1.392(3); C(1)-C(6): 1.392(3); C(2)-C(3): 1.390(4); C(3)-C(4): 1.383(4); C(4)-C(5): 1.383(4); C(5)-C(6): 1.386(4); C(7)-C(12): 1.393(4); C(7)-C(8): 1.398(3); C(8)-C(9): 1.395(4); C(9)-C(10): 1.376(4); C(10)-C(11): 1.377(4); C(11)-C(12): 1.391(4); Si(3)-P(1)-Si(1): 102.06(4); Si(3)-P(1)-Sn(1): 91.58(4); Si(1)-P(1)-Sn(1): 91.01(4); Si(2)-P(2)-Si(4): 102.14(4); Si(2)-P(2)-Sn(1): 90.71(4); Si(4)-P(2)-Sn(1): 91.79(4); C(7)-Sn(1)-C(1): 104.04(9); C(7)-Sn(1)-P(2): 113.44(7); C(1)-Sn(1)-P(2): 109.86(7); C(7)-Sn(1)-P(1): 110.57(7); C(1)-Sn(1)-P(1): 113.48(7); P(2)-Sn(1)-P(1): 105.66(4); C(14)-Si(1)-C(13): 107.60(13); C(14)-Si(1)-P(1): 106.32(9); C(13)-Si(1)-P(1): 111.41(9); C(14)-Si(1)-Si(2): 109.07(10); C(13)-Si(1)-Si(2): 110.95(10); P(1)-Si(1)-Si(2): 111.29(4); C(16)-Si(2)-C(15): 107.18(12); C(16)-Si(2)-P(2): 105.87(9); C(15)-Si(2)-P(2): 112.44(9); C(16)-Si(2)-Si(1): 109.29(9); C(15)-Si(2)-Si(1): 110.72(9); P(2)-Si(2)-Si(1): 111.11(5); C(17)-Si(3)-C(18): 107.90(13); C(17)-Si(3)-P(1): 111.77(10); C(18)-Si(3)-P(1): 105.68(9); C(17)-Si(3)-Si(4): 110.87(9); C(18)-Si(3)-Si(4): 109.15(10); P(1)-Si(3)-Si(4): 111.25(4); C(19)-Si(4)-C(20): 107.69(12); C(19)-Si(4)-P(2): 106.59(9); C(20)-Si(4)-P(2): 111.21(9); C(19)-Si(4)-Si(3): 108.76(9); C(20)-Si(4)-Si(3): 111.21(9); P(2)-Si(4)-Si(3): 11.19(4); C(2)-C(1)-C(6): 118.5(2); C(2)-C(1)-Sn(1): 120.81(18); C(6)-C(1)-Sn(1): 120.18(18); C(3)-C(2)-C(1): 120.9(2); C(4)-C(3)-C(2): 119.8(2); C(3)-C(4)-C(5): 120.0(2); C(6)-C(5)-C(4): 120.1(3); C(5)-C(6)-C(1): 120.7(2); C(12)-C(7)-C(8): 118.3(2); C(12)-C(7)-Sn(1): 120.30(18); C(8)-C(7)-Sn(1): 121.01(18); C(9)-C(8)-C(7): 120.3(2); C(10)-C(9)-C(8): 120.4(2); C(9)-C(10)-C(11): 120.1(2); C(10)-C(11)-C(12): 120.0(3); C(11)-C(12)-C(7): 121.0(2).

The P-Si bond lengths of this cage are similar to the Si-P bond lengths in the cage $P_2Si_5Me_{10}$ that are around 2.260 Å [40].

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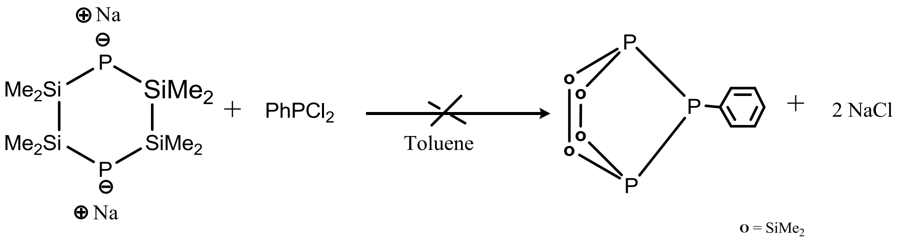
[40] Kollegger. G. M.; Katzenbeisser. U.; Hassler. K.; Krüger. C.; Brauer. D.; Gielen. R.; J. Organomet. Chem., **1997**, 543, 106.

Table 5: Crystal data and structure refinement for $P_2Si_4Me_8SnPh_2$.

Empirical formula	C_{20} H_{34} P_2 Si_4Sn
Formula weight	567,46
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.8075(18) Å alpha = 87.75(3) deg. b = 10.018(2) Å beta = 80.75(3) deg. c = 16.861(3) Å gamma = 66.33(3) deg.
Volume	1341,9(5) Å ^{3}
Z, Calculated density	2, 1.404 Mg/m^3
Absorption coefficient	1.255 mm^{-1}
F(000)	580
Crystal size	0.34 x 0.30 x 0.21 mm
Theta range for data collection	2.22 to 26.37 deg.
Limiting indices	-10<=h<=10, -12<=k<=12, -21<=l<=20
Reflections collected / unique	10798 / 5394 [R(int) = 0.0197]
Completeness to theta = 22.50	98.6%
Absorption correction	SADABS
Max. and min. transmission	0.7785 and 0.6749
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5394 / 0 / 252
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0642
R indices (all data)	R1 = 0.0289, wR2 = 0.0640
Largest diff. peak and hole	0.870 and -0.412 e. Å $^{-3}$

3.2.2.11- Reaction of $[P_2Si_4Me_8]^{2-}$ with Cl_2PPh



The reaction of $[P_2Si_4Me_8]^{2-}$ with Cl_2PPh in a ratio of 1:1 was excepted to give P_3Si_4MePh, in which a P-atom connects the two P-atoms of the dianion. The dianion dissolved in DME/toluene was added to a toluene solution of Cl_2PPh at low temperature. The ^{31}P-NMR spectrum (Figure 42) displayed a triplet at 17,7 ppm (J_{PP}=306 Hz) and a doublet at -145,7 ppm (J_{PP}= 307 Hz) typical for a P_3-atom arrangement. Another signal at -250,0 ppm was present, typical signal from the cage $P_2Si_6Me_{12}$.

Unfortunately crystals could not be obtained to confirm the characterization.

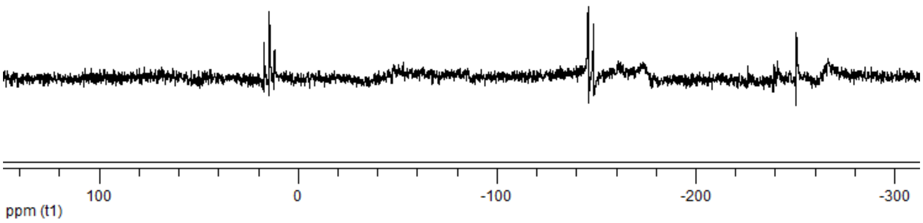
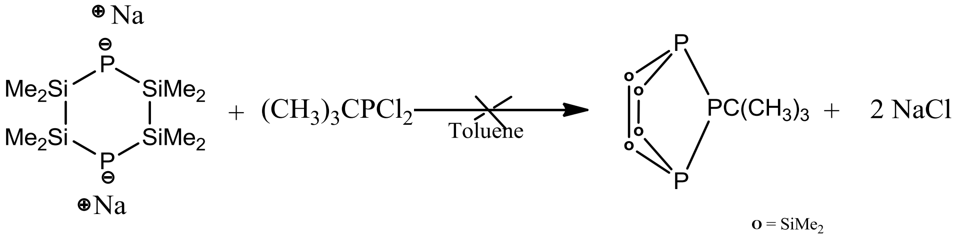


Figure 42: ^{31}P-NMR spectrum of the reaction mixture.

3.2.2.12- *Reaction of* $[P_2Si_4Me_8]^{2-}$ *with* $(CH_3)_3CPCl_2$



In this attempt the target cage was $P_3Si_4Me_8C(CH_3)_3$ consisting again of a P-atom connected to the P-atoms of the dianion $[P_2Si_4Me_8]^{2-}$.

The dianion was added dropwise to a solution of $(CH_3)_3CPCl_2$ in toluene at low temperature. The ^{31}P-NMR (Figure 43) from the orange solution formed displayed signals that match with the desired cage, a triplet at 43,2 ppm (J_{PP}= 308 Hz) from the P-$C(CH_3)_3$ atom and a doublet at -156,6 ppm (J_{PP}= 309 Hz) from the other P-atoms. Another signal of unknown origin at 66,2 ppm was displayed.

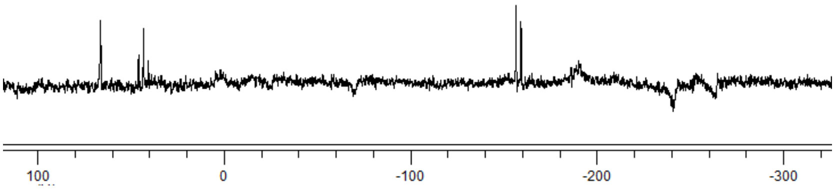
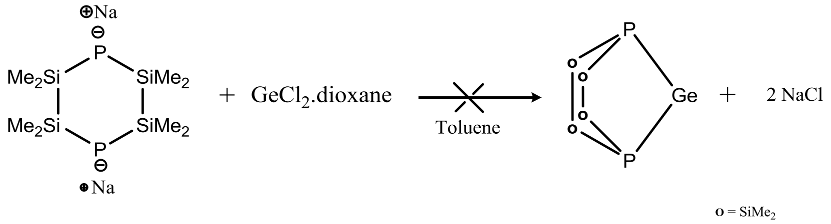


Figure 43: ^{31}P-NMR spectrum of the reaction mixture.

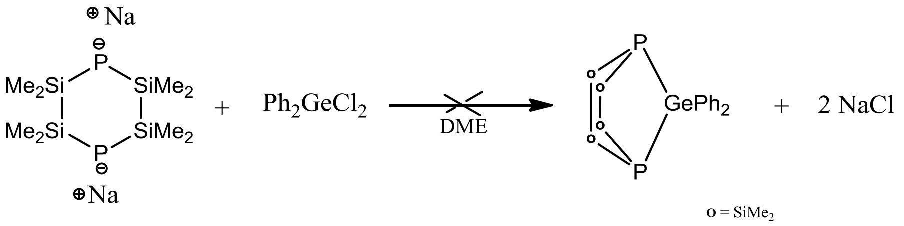
In the ^{1}H-NMR spectrum the displayed signals can also match whith the target cage. A signal found at 0,45 ppm can be from the $SiMe_2$ groups and the signal found at 3,44 ppm can be from the $C(CH_3)_3$ group. Here also the characterization of the cage could not be completed because crystals didn't grow from the solution.

3.2.2.13- *Reaction of [$P_2Si_4Me_8$]$^{2-}$ with $GeCl_2$.dioxane*



The expectation here was that the reaction of [$P_2Si_4Me_8$]$^{2-}$ with $GeCl_2$.dioxane in a molar ratio of 1:1 gives the cage $P_2Si_4Me_8Ge$, which consist of a germanium atom connected to the P-atoms of the dianion. [$P_2Si_4Me_8$]$^{2-}$ was added dropwise to a solution of $C_4H_8Cl_2GeO_2$ at low temperature. The ^{31}P-NMR spectrum of the solution showed many signals, between them the cage $P_2Si_6Me_{12}$. No crystals suitable for x-ray measurements could be obtained neither from toluene, DME, heptain or hexane.

3.2.2.14- *Reaction of [$P_2Si_4Me_8$]$^{2-}$ with Ph_2GeCl_2*



The aim of this reaction was to form the cage $P_2Si_4Me_8GePh_2$. A DME solution of the dianion [$P_2Si_4Me_8$]$^{2-}$ was added to a solution of Ph_2GeCl_2. The ^{31}P-NMR spectrum of the reaction mixture showed two signals at -238,2 ppm and -107,6 ppm. The target cage didn't form because ^{1}H-NMR spectrum displayed no signals typical for the phenyl groups.

4- Experimental Part

4.1- Analytical methods

4.1.1- 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, and ^{19}F 282.17 MHz). Shifts are reported in ppm down-field from TMS (tetramethylsilane) and are referenced to solvent residual signal. When ^{29}Si-NMR 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 sometimes used[41, 42, and 43]. To observe quarternary silicon atoms bonded to hydrogen or halogen DEPT and standard pulse sequences were used.

4.1.2- Elemental analysis

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

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[41] Morris, G.A.; Freeman R.; J. Am. Chem. Soc., **1979**, 101, 761.

[42] Helmer, B.J.; West, R.; Organometallics, **1962**,1,878.

[43] Blinka, T.A.; Helmer, B.J.; West, R.; Adv. Organomet. Chem., **1984**, 23, 194, 215.

4.1.3- X-Ray Structure determination

For x-ray structure determination 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 Kα radiation (0.7103 Å). The data were reduced to Fo^2 and corrected for absorption effects with SAINT[44] and SADABS[45], respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97)[46]. 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.

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

[45] Blessing, R.H.; Acta Crystallogr. A., **1995**, 51, 35.; SADABS, Version 2.1.; Bruker-AXS, Madison, WI, **1998**.

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

4.2- Syntheses

4.2.1- General synthetic methods

All syntheses and manipulations were carried out under an inert atmosphere of N2 by standing Schlenk techniques or in a nitrogen filled glove box MBRAUN Unilab, supplied by M. Braun GmbH. Solvents were distilled from sodium prior to use. Chemical substances used as starting materials were prepared following literature procedures.

4.2.2- Synthesis of sodium potassium phosphanide

4.2.2.1- Preparation of sodium/potassium alloy

In a three necked-flask, small pieces of sodium and potassium were slowly heated with a heat gun until a liquid metal alloy formed. The alloy was stored under DME. The exact amount of sodium and potassium is specified in the description of the syntheses of the individual compounds.

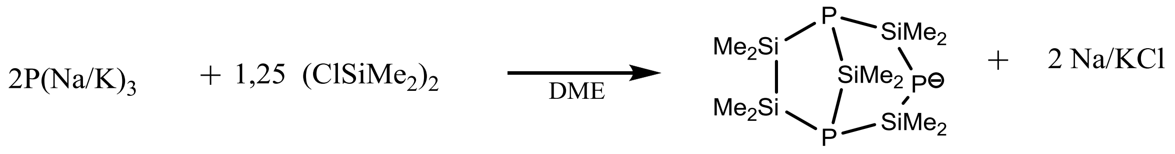
4.2.2.2- Preparation of P(Na/K)$_3$

$$\mathrm{P} \quad + \quad 3\,(\mathrm{Na/K}) \longrightarrow \mathrm{P}^{3-}\,(\mathrm{Na/K})_3^{-}$$

In a three-neck flask, the mixture of Na/K alloy and DME was heated under reflux until the DME turned blue. Red phosphorous was then added and the mixture was refluxed over 48 hours. A dark suspension was formed.

4.2.3- *Reactions with $P(Na/K)_3$*

4.2.3.1- *Synthesis of $[P_3Si_5Me_{10}]^-$ from $Cl_2Si_2Me_4$ and $P(Na/K)_3$*



P_{red}	5 g	30,97 g/mol	16,14 mmol
Na	5,5 g	22,99 g/mol	23,92 mmol
K	9,38 g	9,09 g/mol	23,92 mmol
$Cl_2Si_2Me_4$	19 g	186,9 g/mol	101,6 mmol

A suspension of sodium potassium phosphanide was prepared from 5g of P_{red} and 14,9g of sodium-potassium alloy (5,52g Na, 9,38g K) in 250ml of DME. Residual sodium and potassium was then removed by amalgamation. A solution of 19g of $Cl_2Si_2Me_4$ in 20ml DME was added at -50°C. After complete addition the reaction mixture was refluxed for 24 hours. The precipitated salts were then separated by filtration and the solvent was reduced to ca. 50ml. The formation of $[P_3Si_5Me_{10}]^-$ was verified by ^{31}P-spectroscopy. Signals at -246,7ppm and -262,6 ppm were observed. The crystal structure of this compound was already obtained by Dr Günter Tekautz during is PhD thesis[47].

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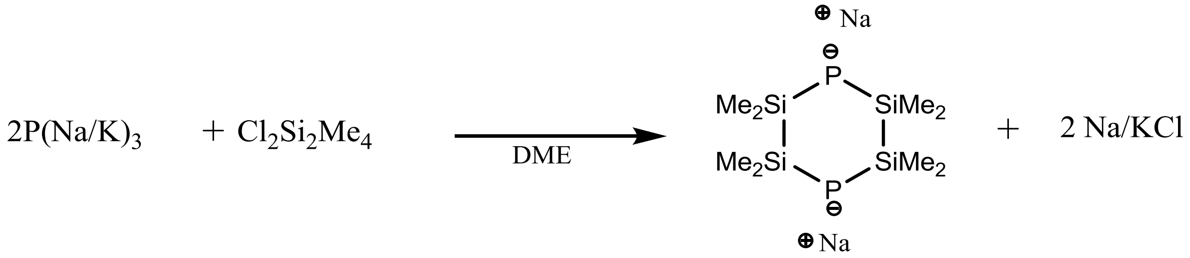
[47] Tekautz, G.; Thesis, T.U. Graz, **2005**, 83.

4.2.3.2- Synthesis of $[P_2Si_4Me_8]^{2-}$ *from* $Cl_2Si_2Me_4$ *and* $P(Na/K)_3$



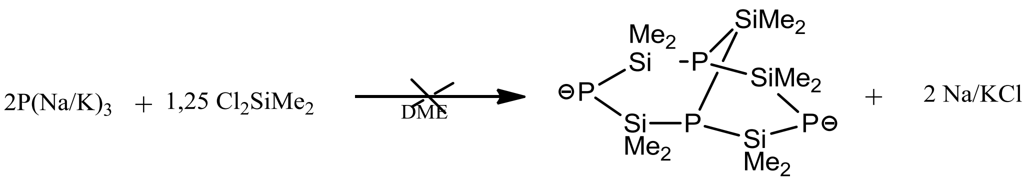
P_{red}	5 g	30,97 g/mol	16,14 mmol
Na	5,5 g	22,99 g/mol	23,92 mmol
K	9,38 g	9,09 g/mol	23,92 mmol
$Cl_2Si_2Me_4$	15 g	186,9 g/mol	80,25 mmol

A suspension of sodium potassium phosphanide was prepared from 5g of P_{red} and 14,9g of sodium-potassium alloy (5,52g Na, 9,38g K) in 250ml DME. The excess of sodium and potassium was removed by amalgamation. A solution of 15g of $Cl_2Si_2Me_4$ in 20ml DME was added dropwise over a period of 30 min at -50°C. After completion the reaction mixture was allowed to slowly warm up to room temperature, and the precipitated salts were separated by filtration. The solvent was then reduced to ca. 50ml and $[P_2Si_4Me_8]^{2-}$ was purified by crystallization from DME at -30°C.

^{31}P $\{^1H\}$-NMR: δ = -302,3 ppm (s)

^{29}Si $\{^1H\}$-NMR: δ=-20,0 ppm (pseudodublet, J= 67Hz)

4.2.3.3- Synthesis of $[P_4Si_5Me_{10}]^{2-}$ from Cl_2SiMe_2 and $P(Na/K)_3$



P_{red}	5 g	30,97 g/mol	16,14 mmol
Na	5,5 g	22,99 g/mol	23,92 mmol
K	9,38 g	9,09 g/mol	23,92 mmol
Cl_2SiMe_2	25,79 g	128,98 g/mol	199,95 mmol

A suspension of sodium potassium phosphanide was prepared from 5g of P_{red} and 14,9g of sodium-potassium alloy (5,52g Na, 9,38g K) in 250ml DME. A solution of 25,79g of Cl_2SiMe_2 in 20ml DME was added dropwise over a period of 50 min at -50°C. After completion the reaction mixture was allowed to slowly warm up to room temperature. The precipitated salts were separated by filtration. The solution was then reduced to ca. 50ml. The ^{31}P-NMR spectrum displayed signals at -219,0 ppm, -228,3ppm, -287,5 ppm and -303,4 ppm. The cage could not be identified, crystals were not obtained.

4.2.3.4- Synthesis of new cages from Ph_2SiCl_2 and $P(Na/K)_3$

$$P(Na/K)_3 \quad + \quad Ph_2SiCl_2 \xrightarrow[\text{DME}]{} \quad ? \quad + \quad 2\ Na/KCl$$

P_{red}	5 g	30,97 g/mol	161,4 mmol
Na	5,5 g	22,99 g/mol	23,92 mmol
K	9,38 g	9,09 g/mol	23,92 mmol
Ph_2SiCl_2	13,6 g	255,0 g/mol	53,33 mmol

A suspension of sodium potassium phosphanide was prepared from 5g of P_{red} and 14,9g of sodium-potassium alloy (5,52g Na, 9,38g K) in 250ml DME. A solution of 13,6g of Ph_2SiCl_2 was added dropwise over a period of 30 min at -80°C. After completion the reaction mixture was allowed to slowly warm up to room temperature. The precipitated salts were separated by filtration. The ^{31}P-NMR spectrum showed a mixture of products, signals were displayed at -212,6 ppm, -218,0ppm, -250,9 ppm, -264,5 ppm, -286,6 ppm, -301,9 ppm and -313,0 ppm. Crystals didn't grown from the solution.

4.2.3.5- Synthesis of new cages from $Cl_2MeSiSi(SiMe_3)_3$ and $P(Na/K)_3$

$$2\ P(Na/K)_3 + Cl_2MeSiSiH_2(SiMe_3)_3 \xrightarrow[\text{DME}]{} \ ? \ + \ 2\ Na/KCl$$

P_{red}	0,28 g	30,97 g/mol	9,04 mmol
Na	0,31 g	22,99 g/mol	13,48 mmol
K	0,53 g	9,09 g/mol	13,48 mmol
$Cl_2MeSiSi(SiMe_3)_3$	5 g	361,0 g/mol	13,85 mmol

A suspension of sodium potassium phosphanide was prepared from 0,28g of P_{red} and 0,84g of sodium-potassium alloy (0,31g Na, 0,53g K) in 50ml DME. DME was removed and 30ml toluene was added. A solution of 5g of $Cl_2MeSiSi(SiMe_3)_3$ dissolved in 10ml of toluene was added dropwise over a period of 30 min at -80°C. After completion the reaction mixture was allowed to slowly warm up to room temperature. The precipitated salts were separated by filtration. The absence of signals in the ^{31}P-NMR spectrum showed that no soluble Si-P compounds had formed.

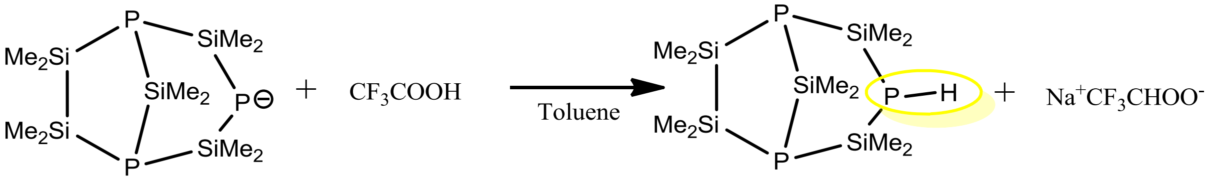
4.2.4- Syntheses of new compounds and new reactions

4.2.4.1- Reactions of [$P_3Si_5Me_{10}$]$^-$

The concentration of the anion present in the solution was determined by titration in H_2O. The concentration obtained was 0,288mol/L. In all the reactions with [$P_3Si_5Me_{10}$]$^-$ 20 ml of the solution was used.

$$\text{P-Na} \quad + \quad H_2O \longrightarrow \text{PH} \quad + \quad \text{NaOH (titrated with HCl (0,1M))}$$

4.2.4.1.1- Reaction with CF_3COOH



[$P_3Si_5Me_{10}$]$^-$	1,81 g	398,73 g/mol	5,76 mmol
CF_3COOH	0,65 g	115,03 g/mol	5,76 mmol

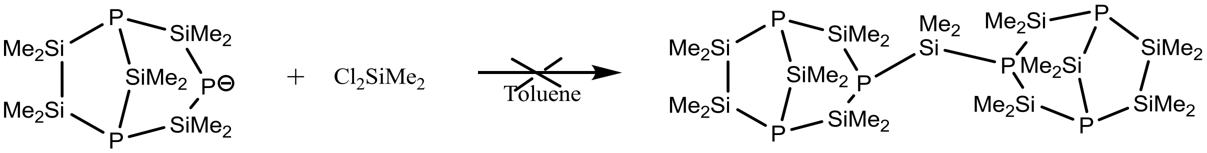
In a 100 ml three-necked flask, 0,65g of CF_3COOH was dissolved in 15ml of toluene and the solution was cooled to -50°C. A toluene/DME solution of [$P_3Si_5Me_{10}$]$^-$ (2,29g ; 5,76 mmol) was added dropwise over a period of 20 min, and the mixture was stirred for 2h. The reaction mixture was slowly warmed up to room temperature. The solution was colourless and a brown precipitate had formed. The precipitate was separated from the solution by decantation. Crystals suitable for x-ray analysis could be grown from heptane at -30°C.

^{31}P {^{1}H}-NMR: δ = -231,1 ppm (J=176Hz), δ= -236,9 ppm (J=186Hz), δ= -240,8 ppm, δ= -246,4 ppm

^{29}Si {^{1}H}-NMR: δ= 14,8 ppm (t, J= 48 Hz), δ= 1,2 ppm (dd, J=44Hz, J=51Hz)

^{1}H-NMR: δ= 0,3 ppm (t, J= 6,7 Hz, $SiMe_2$), δ= 0,4 ppm (t, J= 6,4 Hz, $SiMe_2$), δ= 0,8 ppm (t, J=5,9 Hz, $SiMe_2$), signal from P-H bond not found.

4.2.4.1.2- *Reaction with Cl_2SiMe_2*

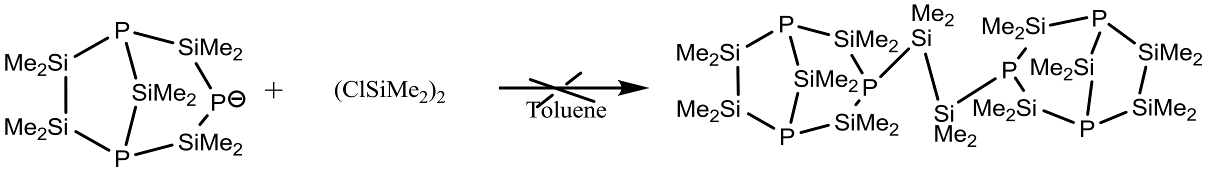


$[P_3Si_5Me_{10}]^-$	1,81 g	398,73 g/mol	5,76 mmol
Cl_2SiMe_2	0,37 g	129,06 g/mol	5,76 mmol

In a 100 ml three-necked flask, 2,28g of $[P_3Si_5Me_{10}]^-$ was dissolved in 20ml toluene and 20ml DME and the solution was cooled to -50°C. A toluene solution of Cl_2SiMe_2 (0,37g; 5,76 mmol) was added dropwise over a period of 20 min, and the mixture was stirred for 2h. The reaction mixture was slowly warmed up to room temperature. The solution showed an orange colour and a precipitate had formed. The precipitate was separated from the solution by decantation. The ^{31}P-NMR spectrum displayed signals at -223,3 ppm, -236,0 ppm, -246,2 ppm, and very week signals at -15,1 ppm and -73,6 ppm which could not be assigned. In the ^{29}Si-NMR spectrum, signals displayed at 26,5ppm, 17,0 ppm, 5,1 ppm -1,7 ppm, -2,5 ppm, -3, 7 ppm,-4,7 ppm and -19,2 ppm also could not be assigned.

All attempts to obtain crystals from the reaction mixture failed.

4.2.4.1.3- Reaction with $Cl_2Si_2Me_4$



$[P_3Si_5Me_{10}]^-$	1,81 g	398,73 g/mol	5,73 mmol
Cl_2SiMe_2	0,53 g	186,9 g/mol	5,73 mmol

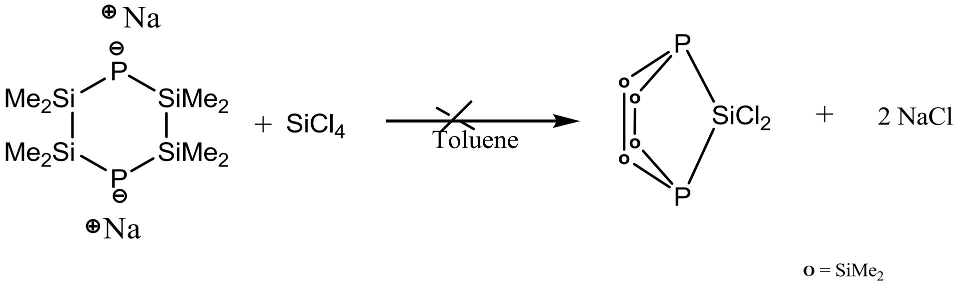
In a 100 ml three-necked flask, 2,28g of $[P_3Si_5Me_{10}]^-$ was dissolved in 20ml toluene and 20 ml DME and the solution was cooled to -50°C. A toluene solution of $Cl_2Si_2Me_4$ (0,53g; 5,76 mmol) was added dropwise over a period of 20 min, and the mixture was stirred for 2h. The reaction mixture was slowly warmed up to room temperature. The solution showed a orange colour and a precipitate had formed. The precipitate was separated from the solution by decantation. The ^{31}P-NMR spectrum displayed signals at -225.9 ppm, -226,0 ppm, -226,6 ppm, -232.5 ppm, -244,4 ppm and -250,0 ppm which could not be assigned. In the ^{29}Si-NMR spectrum signals that were displayed at 24,9 ppm, 15,8 ppm, 4,9 ppm, -2,8 ppm, 0,1 ppm, -2,1 ppm,-2,7 ppm and -19,3 ppm could also not be assigned.

Despite many attempts, no crystalline fraction could be obtained.

4.2.4.2- *Reactions of [$P_2Si_4Me_8$]$^{2-}$*

The concentration of the dianion present in the DME solution was determined by titration in H_2O. The concentration obtained was 0,305mol/L.

4.2.4.2.1- *Reaction with $SiCl_4$*

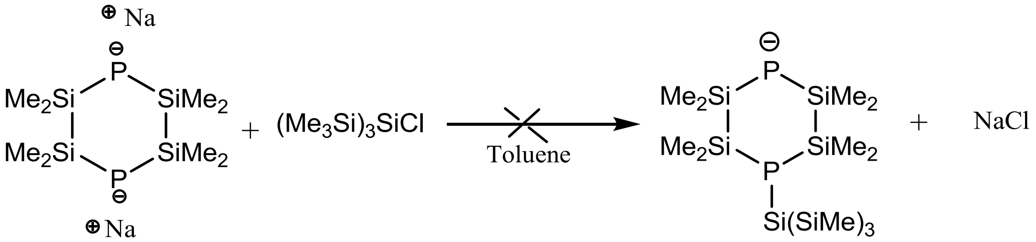


[$P_2Si_4Me_8$]$^{2-}$	0,9 g (10ml)	294,26 g/mol	3,05 mmol
$SiCl_4$	0,52 g	69,8 g/mol	3,05 mmol

In a 100 ml three-necked flask, 0,52g of $SiCl_4$ dissolved in 15 ml toluene was added dropwise to a solution of [$P_2Si_4Me_8$]$^{2-}$ (0,9g ; 3,05 mmol in 15 ml toluene and 15 ml DME) at -50°C. The reaction was stirred for 1h at -50°C. The reaction mixture was then slowly warmed up to room temperature, showing an intensely orange colour. A precipitate had formed which was separated from the solution by decantation.

The ^{31}P-NMR spectrum displayed a signal at -206,3 ppm. In the ^{29}Si-NMR spectrum signals were displayed at 15,4 ppm (s) and 25,1 ppm (s). As both signals are singlets, no Si-P bond has formed. Unfortunately a crystalline fraction could not be obtained to confirm the presence of the desired product by x-ray diffraction.

4.2.4.2.2- Reaction with $(Me_3Si)_3SiCl$

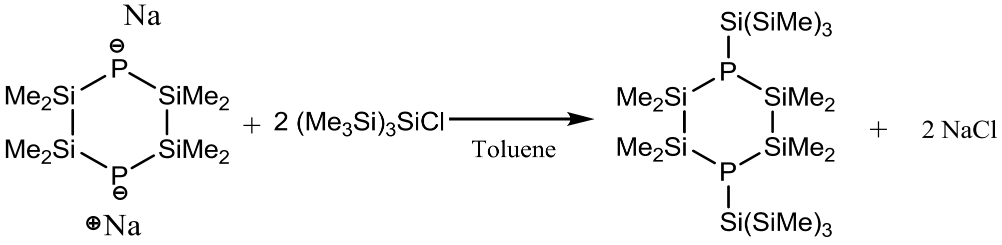


$[P_2Si_4Me_8]^{2-}$	2,0 g (22,3ml)	294,26g/mol	6,80 mmol
$(Me_3Si)_3SiCl$	1,94 g	285,65g/mol	6,80 mmol

In a 100 ml three-necked flask, 1,94g of Si_4Me_9Cl dissolved in 15 ml toluene and 15 ml DME were added dropwise to a solution of $[P_2Si_4Me_8]^{2-}$ (2,0g ; 6,80 mmol in 15 ml toluene) at -50°C. The mixture was stirred for 2h at -50°C. The reaction mixture was then slowly warmed up to room temperature. The solution was yellow and a white precipitate had formed, which was separated from the solution by decantation.

The ^{31}P {^1H}-NMR spectrum showed signals at -212,0 ppm, -259,4 ppm, -265,7 ppm, -271,8 ppm and -314,0 ppm. The signals at -271,8 ppm and -314,0 can be from the desired product, signals at -212,0 ppm and -259,4 are from $P_2Si_5Me_{10}$ and $P_2Si_{12}Me_{14}$ respectively. As crystals could not be obtained from the solution the compounds could not be correctly identified.

4.2.4.2.3- Reaction with $(Me_3Si)_3SiCl$



$[P_2Si_4Me_8]^{2-}$	2,0 g (22,3ml)	294,26 g/mol	6,80 mmol
$(Me_3Si)_3SiCl$	2,30 g	285,65 g/mol	13,60 mmol

In a 100 ml three-necked flask, Si_4Me_9Cl (2,30g) dissolved in 15 ml toluene was added dropwise to a solution of $[P_2Si_4Me_8]^{2-}$ (2,0g; 6,80 mmol in 15 ml toluene and 15 ml DME) at -50°C. The mixture was stirred for 2h at -50°C and then allowed to slowly warm up to room temperature. The salts were separated from the solution by decantation. The structure was identified by ^{31}P {^1H}-NMR and ^{29}Si{^1H}-NMR. Crystals grown from heptane at -30°C were suitable for x-ray analysis.

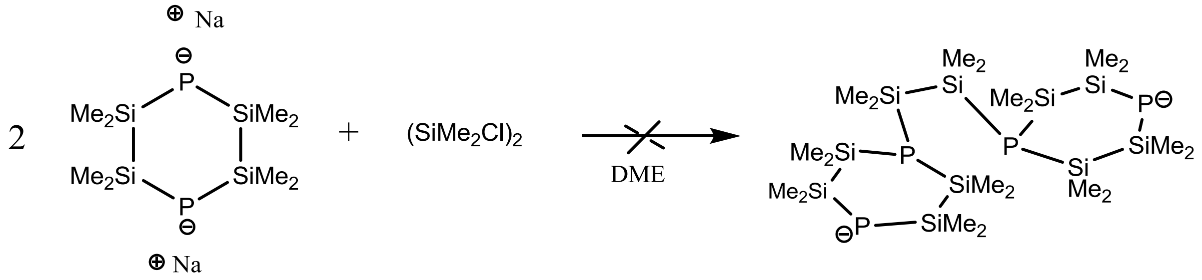
Elemental Analisis C_{26} H_{78} P_2 Si_{12} (789.90), calc/found: C: 39,31/39,54%, H: 9,80/9,95%.

^{31}P {^1H}-NMR: δ = -269, 5 ppm

^{29}Si {^1H}-NMR: δ= 0,7 (s, $SiMe_3$), δ= -14,6 ppm(pseudotriplet, $SiMe_2$), δ= -83,5ppm (d, Si-P);

^1H-NMR: δ= 0,1 ppm (s, $SiMe_2$), δ= 1,9 ppm(s, $SiMe_3$)

4.2.4.2.4- *Reaction with* $(SiMe_2Cl)_2$



$[P_2Si_4Me_8]^{2-}$	0,5 g (5,5ml)	294,26 g/mol	1,69 mmol
$Si_2Me_4Cl_2$	0,16 g	186,9 g/mol	0,85 mmol

In a 100 ml three-necked flask, 0,16g of $(SiMe_2Cl)_2$ dissolved in 15 ml DME was added dropwise to a solution of $[P_2Si_4Me_8]^{2-}$ (0,5g ; 1,69 mmol in 15 ml toluene and 15 ml DME) at -50°C. The mixture was stirred for 2h at -50°C and then allowed to slowly warm up to room temperature. In the intensely orange solution a precipitate had formed, which was separed from the solution by decantation. The ^{31}P-NMR spectrum of the solution showed the typical signal at -250,4 ppm of the cage $P_2Si_6Me_{12}$ which was already identified by Dr. Günter Tekautz in his PhD thesis[47]. Additional signals were displayed at -223,4 ppm, -242,0 ppm, -246,9 ppm, -249,0 ppm which could not be assigned.

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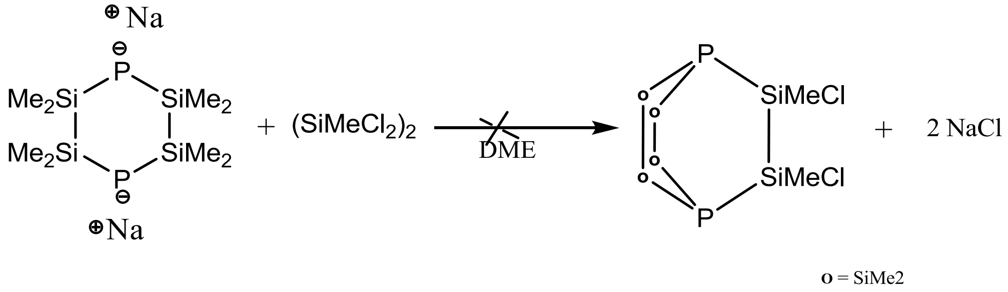
[47] Tekautz, G.; Thesis, T.U. Graz, **2005**, 83.

4.2.4.2.5- Reaction with ($Cl_2MeSi)_2$



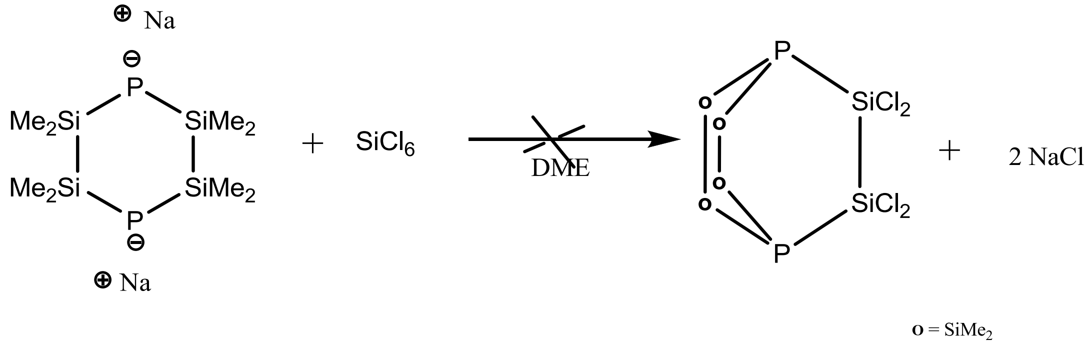
$[P_2Si_4Me_8]^{2-}$	0,5 g (5,5ml)	294,26 g/mol	1,69 mmol
$(Cl_2MeSi)_2$	0,389 g	229,42 g/mol	1,69 mmol

In a 100 ml three-necked flask, 0,389g of $(Cl_2MeSi)_2$ dissolved in 15 ml DME was added dropwise to a solution of $[P_2Si_4Me_8]^{2-}$ (0,5g ; 1,69 mmol in 15 ml toluene and 15 ml DME) at -50°C. The mixture was stirred for 1h at -50°C and then allowed to slowly warm up to room temperature. The salts were separated from the yellow solution by decantation. The compound was probably present in the solution but crystals could not be obtained to complete the characterization.

^{31}P {^1H}-NMR: δ = -243, 3 ppm (s), δ= -213,9 ppm (s)

^{29}Si {^1H}-NMR: δ= 27,8 ppm (t), δ= -3,5 ppm (d), δ= -11,2 ppm (d); δ= -18,8 ppm (s), δ=-21,2 ppm (d)

4.2.4.2.6- Reaction with Si_2Cl_6



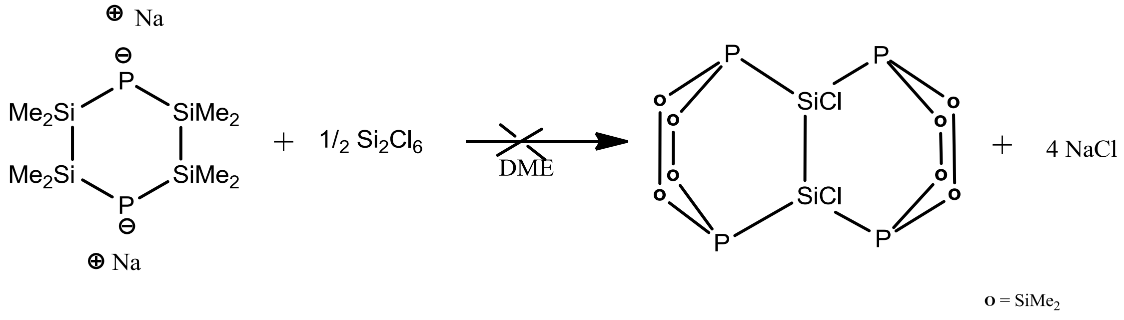
$[P_2Si_4Me_8]^{2-}$	0,5 g (5,5ml)	294,26 g/mol	1,69 mmol
Si_2Cl_6	0,46 g	268,86 g/mol	1,69 mmol

In a 100 ml three-necked flask, 0,46g of Si_2Cl_6 dissolved in 15 ml DME was added dropwise to a solution of $[P_2Si_4Me_8]^{2-}$ (0,5g ; 1,69 mmol in 15 ml toluene and 15 ml DME) at -50°C. After complete addition the mixture was stirred for 1h at -50°C and then allowed to slowly warm up to room temperature. The salts were separated from the orange solution by decantation. Different solvents as DME, heptane, toluene and hexane were unsuccessfully used to obtain crystals.

^{31}P {^1H}-NMR: δ = -168,9 ppm (s), δ= -109,7 ppm (s)

^{29}Si {^1H}-NMR: δ= 29,6 ppm (s), δ= 19,2 ppm (d), δ= 16,4 ppm (s)

4.2.4.2.7- Reaction with Si_2Cl_6



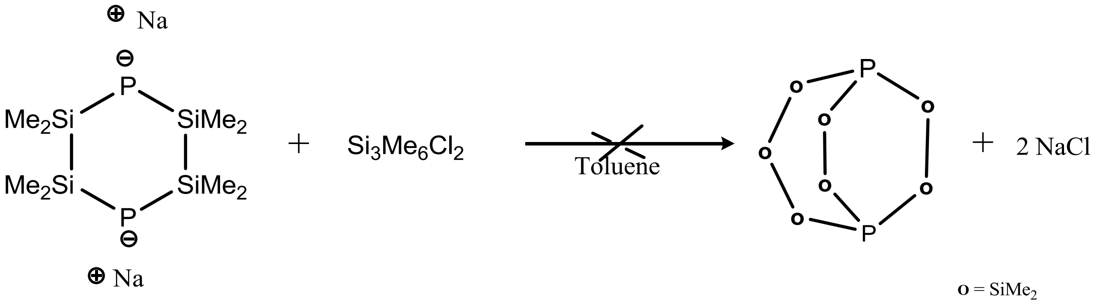
$[P_2Si_4Me_8]^{2-}$	1,0 g (11,1ml)	294,26 g/mol	3,40 mmol
Si_2Cl_6	0,46 g	268,86 g/mol	1,70 mmol

In a 100 ml three-necked flask, 1,83g of Si_2Cl_6 dissolved in 30 ml DME was added dropwise to a solution of $[P_2Si_4Me_8]^{2-}$ (0,5g ; 1,69 mmol in 30 ml toluene and 30 ml DME) at -50°C. The mixture was stirred for 1h at -50°C. The reaction mixture was slowly warmed up to room temperature. The solution was red and an orange precipitate had formed. The salts were separated from the solution by decantation. As just singlets were found in the ^{29}Si-NMR spectrum, no Si-P bonds have formed. DME, toluene, heptane and hexane were unsuccessfully used to obtain crystals.

^{31}P {^{1}H}-NMR: δ = -168,9 ppm

^{29}Si {^{1}H}-NMR: δ= 25,8 ppm (s), δ= 18,9 ppm (s), δ=16,1 ppm (s)

4.2.4.2.8- Reaction with $Cl_2Si_3Me_6$



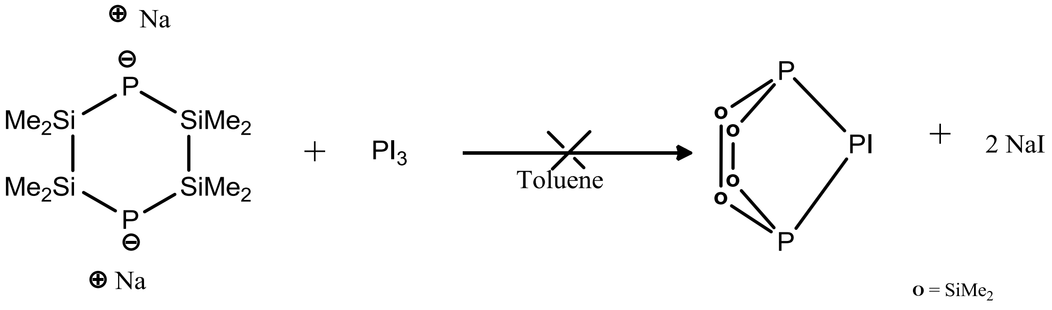
$[P_2Si_4Me_8]^{2-}$	0,5 g (5,5ml)	294,26 g/mol	1,69 mmol
$Cl_2Si_3Me_6$	0,42 g	245,14 g/mol	1,69 mmol

In a 100 ml three-necked flask, 0,5g of $[P_2Si_4Me_8]^{2-}$ dissolved in 15 ml toluene and 15 ml DME was added dropwise to a solution of $Cl_2Si_3Me_6$ (0,42g; 1, 69 mmol in 15 ml toluene) at -50°C. The mixture was stirred for 1h at -50°C. The reaction mixture was slowly warmed up to room temperature. The salts were separated from the orange solution by decantation. No crystals could be grown from hexane.

^{31}P {^1H}-NMR: δ = -262,0 ppm

^{29}Si {^1H}-NMR: δ= -21,4 ppm (s), δ= -19,1 ppm (s), δ= -16,9 ppm (d), δ= -12,0 ppm (s)

4.2.4.2.9- *Reaction with PI_3*



$[P_2Si_4Me_8]^{2-}$	0,5 g (5,5ml)	294,26 g/mol	1,69 mmol
PI_3	0,69 g	411,67 g/mol	1,69 mmol

In a 100 ml three-necked flask, 0,5g of $[P_2Si_4Me_8]^{2-}$ dissolved in 15 ml toluene and 15ml DME was added dropwise to a solution of PI_3 (0,69g; 1, 69 mmol in 15 ml toluene) at -50°C. The mixture was stirred for 1h at -50°C and then was allowed to slowly warm up to room temperature. The salts were separated from the orange solution by decantation. The ^{31}P-NMR spectrum of the solution showed at -250,0 ppm the typical signal of the cage $P_2Si_6Me_{12}$[47] already known. Other signals were displayed at -7,4 ppm, -10,6 ppm, -11,4 ppm and -12,8 ppm. In the ^{29}Si-NMR spectrum signals at 2,9 ppm, 1,0 ppm, -11,8 ppm -19,3 ppm and -21,6 ppm were observed which could not be assigned. All attempts to obtain crystals from the reaction mixture failed.

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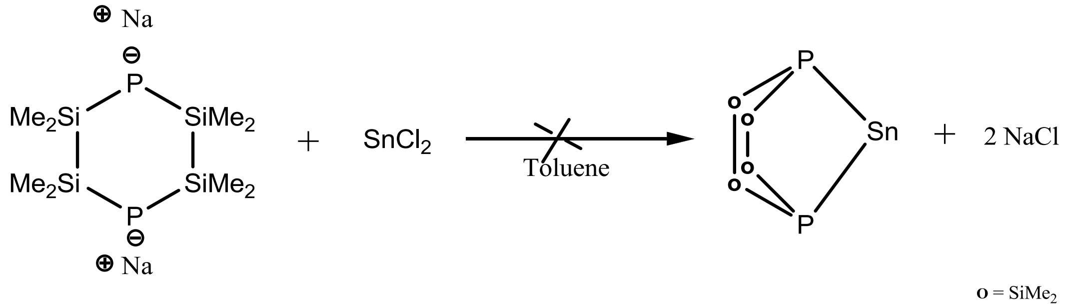
[47] Tekautz, G.; Thesis, T.U Graz, **2005**, 83.

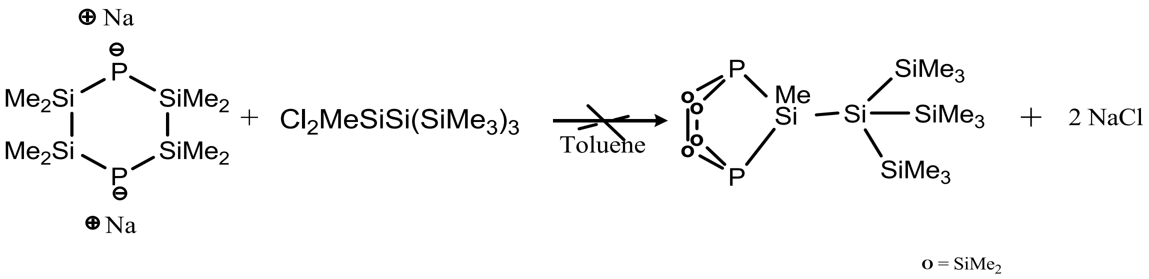
4.2.4.2.10- Reaction with $SnCl_2$



$[P_2Si_4Me_8]^{2-}$	0,5 g (5,5ml)	294,26 g/mol	1,69 mmol
$SnCl_2$	0,32 g	189,51 g/mol	1,69 mmol

In a 100 ml three-necked flask, 0,5g of $[P_2Si_4Me_8]^{2-}$ dissolved in 15 ml toluene and 15 ml DME was added dropwise to a solution of $SnCl_2$ (0,32g; 1, 69 mmol in 15 ml toluene) at -50°C and then stirred for 1h at -50°C. The reaction mixture was then allowed to slowly warm up to room temperature. The solution was dark brown and a soft precipitate had formed. The solution and the precipitate were separated by decantation. The ^{31}P-NMR spectrum of the solution showed no signals. Evidently, just polymeric insoluble compounds had formed.

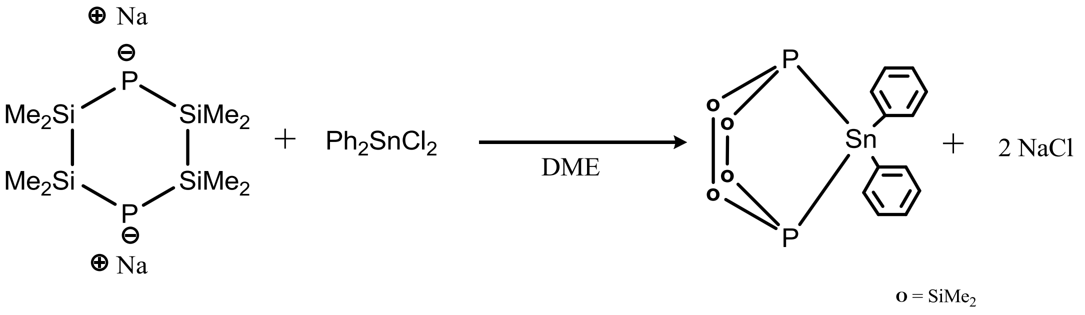
4.2.4.2.11- *Reaction with $Cl_2MeSiSi(SiMe_3)_3$*



$[P_2Si_4Me_8]^{2-}$	0,5 g (5,5ml)	294,26 g/mol	1,69 mmol
$Cl_2MeSiSi(SiMe_3)_3$	1,23 g	361,3 g/mol	1,69 mmol

In a 100 ml three-necked flask, 0,5g of $[P_2Si_4Me_8]^{2-}$ dissolved in 15 ml toluene and 15 ml DME was added dropwise to a solution of $Cl_2MeSiSi(SiMe_3)_3$ (1,23g ; 1,69 mmol in 15 ml toluene) at -50°C. The mixture was stirred for 1h at -50°C and then was allowed to slowly warm up to room temperature. The salts were separated from the orange solution by decantation. The ^{31}P-NMR spectrum displayed signals at -207,3 ppm, -213,0 ppm, -231,9 ppm and -257,3 ppm , the ^{29}Si-NMR spectrum signals at -9,3 ppm, -10,8 ppm and -16,1 ppm which could not be assigned. No crystals could be obtained from various solvents.

4.2.4.2.12- *Reaction with Ph_2SnCl_2*



$[P_2Si_4Me_8]^{2-}$	1,0 g (11,1ml)	294,26 g/mol	1,69 mmol
Ph_2SnCl_2	0,76 g	223,6 g/mol	1,69 mmol

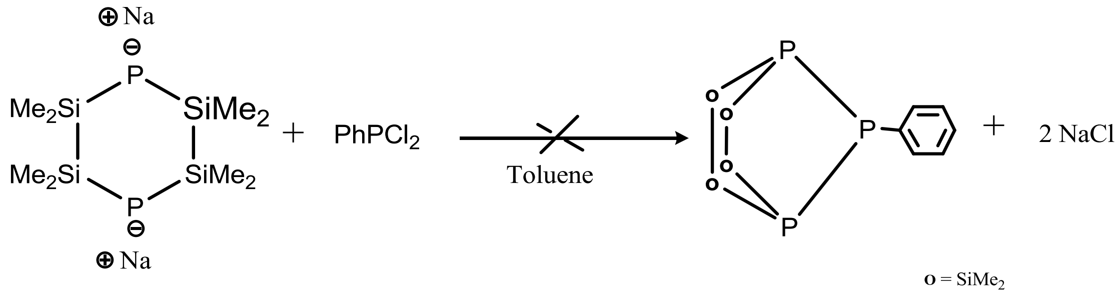
In a 100 ml three-necked flask, 1,0g of $[P_2Si_4Me_8]^{2-}$ dissolved in 15 ml DME were added dropwise to a solution of Ph_2SnCl_2 (0,76g ; 1,69 mmol in 15 ml DME) at -50°C. The mixture was stirred for 1h at -50°C then the reaction mixture was slowly allowed to warm up to room temperature. The salts were separated from the yellow solution by decantation. Crystals were obtained from DME solution at -30°C with a quality suitable for x-ray diffraction experiments.

^{31}P {^1H}-NMR: δ= -232,5 ppm

^{29}Si {^1H}-NMR: δ= -1,2 ppm (d, J=68Hz, by-product), δ= -11,1 ppm (d, J=53Hz, by-product), δ= -24,6 ppm (d, J=37Hz, $SiMe_2$)

^1H-NMR: δ=0,2 ppm (24H, $SiMe_2$); δ= 7,1 ppm (10H, CH)

4.2.4.2.13- *Reaction with $PhPCl_2$*



$[P_2Si_4Me_8]^{2-}$	1,0 g (11,1ml)	294,26 g/mol	1,69 mmol
$PhPCl_2$	0,4 g	118,87 g/mol	1,69 mmol

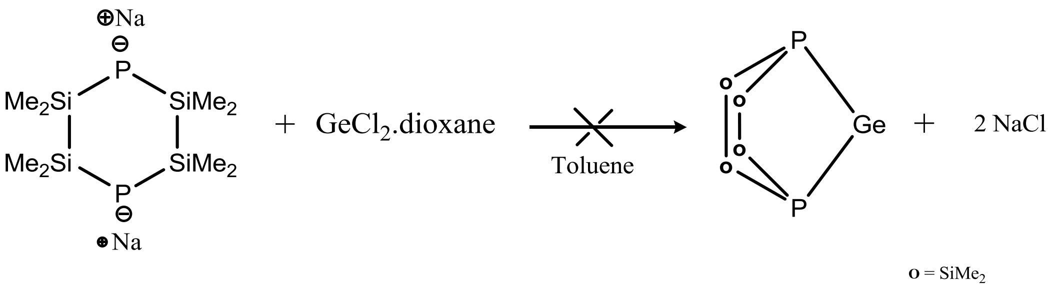
In a 100 ml three-necked flask, 1,0g of $[P_2Si_4Me_8]^{2-}$ dissolved in 15 ml toluene and 15 ml DME was added dropwise to a solution of $PhPCl_2$ (0,4g; 1,69 mmol in 15 ml toluene). The mixture was stirred for 1h at -50°C, and then was allowed to slowly warm up to room temperature. The salts were separated from the yellow solution by decantation. The reaction didn't work because no signals of the phenyl group were displayed in the ^1H-NMR spectrum. Crystals could not be obtained from solvents such as DME, heptane, toluene or hexane, neither at -30°C nor at -80°C.

^{31}P {^1H}-NMR: δ= -250,0 ppm (s), δ = -145,7 ppm (d, J_{PP}= 307 Hz), δ= 17,7 ppm (t, J_{PP}= 306 Hz)

^{29}Si {^1H}-NMR: δ= -18,9 ppm (s), δ= -21,3 ppm (s)

^1H-NMR: δ= 0,516 ppm (d)

4.2.4.2.14- *Reaction with $GeCl_2$.dioxane*



$[P_2Si_4Me_8]^{2-}$	0,5 g (5,5ml)	294,26 g/mol	1,69 mmol
$GeCl_2$.dioxane	0,79 g	231,62 g/mol	1,69 mmol

In a 100 ml three-necked flask, 0,5g of $[P_2Si_4Me_8]^{2-}$ dissolved in 15 ml toluene and 15 ml DME was added dropwise to a solution of $C_4H_8Cl_2GeO_2$ (0,79g; 1, 69 mmol in 15 ml toluene) at -50°C. The mixture was stirred for 1h at -50°C, and was then allowed to slowly warm up to room temperature. The precipitate was separated from the orange solution by decantation. The ^{31}P-NMR spectrum of the solution displayed the typical signal of the cage $P_2Si_6Me_{12}$[47] at -250,4 ppm, besides signals at -185,4 ppm, -226,0 ppm and -241 ppm, which could not be assigned.

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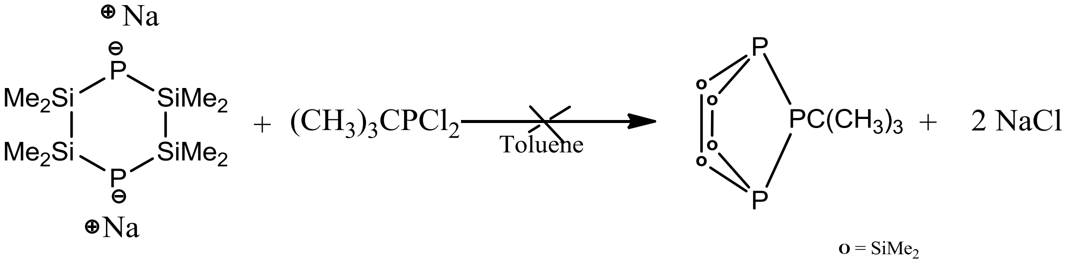
[47] Tekautz, G.; Thesis, T.U. Graz, **2005**, 83.

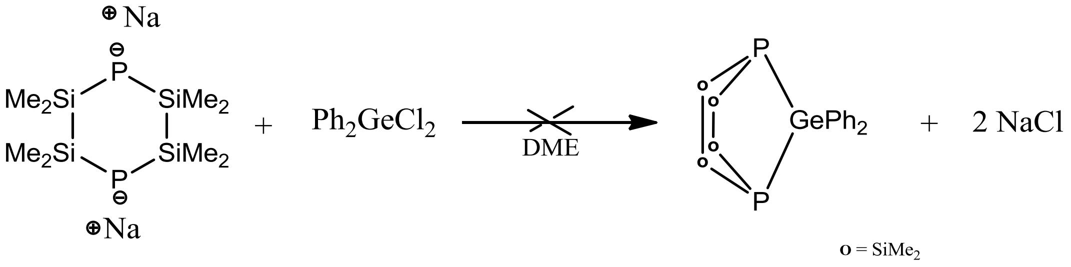
4.2.4.2.15- *Reaction with $(CH_3)_3CPCl_2$*



$[P_2Si_4Me_8]^{2-}$	0,5 g	294,26 g/mol	1,69 mmol
$(CH_3)_3CPCl_2$	0,25 g	146,87 g/mol	1,69mmol

In a 100 ml three-necked flask, 0,5g of $[P_2Si_4Me_8]^{2-}$ dissolved in 15 ml toluene and 15 ml DME was added dropwise to a solution of $(CH_3)_3CPCl_2$ (0,25g; 1, 69 mmol in 15 ml toluene) at -50°C. The mixture was stirred for 1h at -50°C, and was then allowed to slowly warm up to room temperature. The orange solution was separated from the precipitate by decantation. The ^{31}P-NMR spectrum of the solution displayed signals at 66,2 ppm (s), 43,2 ppm (t, J_{PP}= 308 Hz) and -156,6 ppm (d, J_{PP}= 309 Hz). The ^{29}Si-NMR spectrum displayed a pseudodoublet at -18,9 ppm and ^{1}H-NMR spectrum showed 2 signals one at 3,4 ppm from the $C(CH_3)_3$ group and other at 0,4 ppm from the $SiMe_2$ groups.The compound was probably present in the solution but crystals could not be obtained to complete the characterization.

4.2.4.2.16- *Reaction with Ph_2GeCl_2*



$[P_2Si_4Me_8]^{2-}$	0,5 g	294,26 g/mol	1,69 mmol
Ph_2GeCl_2	0,5 g	299,63 g/mol	1,69mmol

In a 100 ml three-necked flask, 0,5g of $[P_2Si_4Me_8]^{2-}$ dissolved in 15 ml DME was added dropwise to a solution of Ph_2GeCl_2 (0,76g; 1,69 mmol in 15 ml DME) at -50°C. The mixture was stirred for 1h at -50°C and was then allowed to slowly warm up to room temperature. The salts were separated from the yellow solution by decantation. The ^{31}P-NMR spectrum of the solution displayed signals at -238,2 ppm and -107,6 ppm which could not be assigned. From the ^{1}H-NMR spectrum we can affirm that the reaction didn't work because just the signals of DME were displayed.

4.2.5- Synthesis of reactants

4.2.5.1- Synthesis of tetrakis(trimethylsilyl)silane:

$$HSiCl_3 + 3\ Me_3SiCl + 6\ Li \longrightarrow HSi(SiMe_3)_3 + Si(SiMe_3)_4 + 6\ LiCl$$

Li	100 g	6,9 g/mol	14,4 mol
Me_3SiCl	686,0 g	108,6 g/mol	6,3 mol
$HSiCl_3$	286,0 g	135,5 g/mol	2,1 mol

In a 3000 ml three-necked flask, 280 ml $HSiCl_3$ (2,1mol, d= 1,342g/ml) and 800 ml of Me_3SiCl (6,3 mol, d= 0,856g/ml) in 220 ml of THF was added dropwise to a suspension of 100g lithium (14,4mol) in 500 ml of THF with vigorous stirring at -10°C. The reaction mixture turned from pale yellow to dark brown. After the addition the reaction mixture was 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 and sublimation. Yields were 366g for $HSi(SiMe_3)_3$ and 203g for $Si(SiMe_3)_4$.

$HSi(SiMe_3)_3$:

$^{29}Si\ \{^1H\}$-NMR: δ= -115,7 ppm (HSi), δ= -12,5 ppm ($SiMe_3$)

$Si(SiMe_3)_4$:

$^{29}Si\ \{^1H\}$-NMR: δ = -135,5 ppm ($Si(SiMe_3)$), δ= -9,8 ppm ($SiMe_3$)

4.2.5.2- Synthesis of 1,2-dichlorotetramethyldisilane

$$Si_2Me_6 \quad + \quad Me_3SiCl \quad \longrightarrow \quad Si_2Me_4Cl_2 \quad + \quad Me_4Si$$

Me_6Si_2	93,6 g	146,39 g/mol	0,64 mol
Me_3SiCl	488,9 g	08,64 g/mol	4,50 mol
$AlCl_3$	3,5 g	133,34 g/mol	0,02 mol
Acetone	4 ml	58,08 g/mol	

93,6g of hexamethyldisilane (0,64mol), 488,9g of trimethylchloroilane (4,50mol) and 3,5g of $AlCl_3$ was placed in to a 1000 ml two-necked flask equipped with a long distillation column and a distillation bridge.

The temperature of the reaction mixture was kept at 70°C with an oil bath. The reaction was running for 72 hours, Me_4Si was continuously removed by distillation. The reaction mixture was then cooled to room temperature and the excess of the aluminiumchloride was deactivated with 4 ml of acetone. A white precipitate had formed, which was separated from the solution by filtration.

The product was purified by distillation under reduced pressure.

Bp= 63-65°C (60mbar)

$^{29}Si\ \{^1H\}$-NMR: $\delta = 17{,}1$ ppm (s)

*4.2.5.3- Synthesis of chlorotris(trimethylsilyl)silane (HypCl)**

$$\mathrm{HSi(SiMe_3)_3} + \mathrm{CCl_4} \longrightarrow \mathrm{ClSi(SiMe_3)_3} + \mathrm{HCCl_3}$$

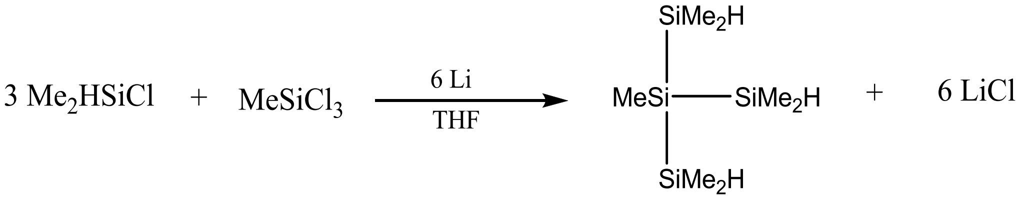
$HSi(SiMe_3)_3$	10,9 g	286,5 g/mol	44,0 mmol
CCl_4	100,0 g	126,13 g/mol	0,7 mol

In a 250ml three-necked flask 10,0g of tris(trimethylsilyl)silane (44,0mmol) was dissolved in 100g (0,7mol) of CCl_4. The solution was stirred under reflux overnight. The solvent was removed and the crude product was purified by vacuum distillation.

Bp: 40°C (0,01mbar)

^{29}Si {^{1}H}-NMR: δ= -14,7 ppm (SiCl), δ= -11,5 ppm ($SiMe_3$)

4.2.5.4- Synthesis of tris(dimethylsilyl)methylsilane



Li	12,9 g	6,91 g/mol	1,6 mol
Me_2HSiCl	88,0 g	94,62 g/mol	930 mmol
Cl_3SiMe	46,3 g	149,48 g/mol	310 mmol

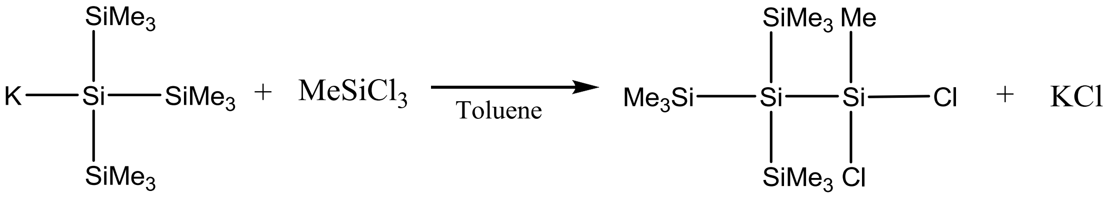
In a 1L three-necked flask 88g of Me_2HSiCl (1,6mol) and 46,3g of Cl_3SiMe was dissolved in 500ml THF. The solution was cooled to -10°C and Li was added in small portions (max 0,5g per piece), while stirring vigorously. After adding all the lithium, the reaction mixture was kept at -10°C and then refluxed for 12 hours.

The excess of lithium was removed by decantation. THF was removed and 150 ml pentane was added (to precipitate LiCl). The salts were removed by filtration and the white precipitate was washed with 15ml of petrol ether. The crude product was purified by vacuum distillation.

Bp= 45°C (0,02mbar)

^{29}Si {^1H}-NMR: δ= -34,9 ppm ($SiMe_2H$), δ= -88,4 ppm (MeSi)

4.2.5.5- Synthesis of 1,1,1-tris(trimethylsilyl)-2,2-dichloro-2-methyldisilane



$KSi(SiMe_3)_3$	1,0 g	361,68 g/mol	3,5 mmol
$MeSiCl_3$	0,5 g	149,48 g/mol	3,5 mmol

In a 100ml three-necked flask, 1,0g (3,5mmol) of $KSi(SiMe_3)_3$ (prepared according to Prof Marschners research group)[48] dissoved in 15ml touluene was added dropwise to a solution of 0,5g $MeSiCl_3$ (3,5mmol) dissolved in 15 ml toluene at -50°C. The reaction mixture was slowly warmed up to room temperature and stirred for further 2h. Toluene was removed and 10ml of pentane was added. After filtration of the salts, pentane was removed and the final product was obtained as a colorless solid.

$^{29}Si\ \{^1H\}$-NMR: δ= 43,3 ppm ($SiMeCl_2$); δ= -9,6 ppm ($SiMe_3$); δ= -120,4 ppm ($Si(SiMe_3)_3$)

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[48] Kayser. Ch.; Thesis, T.U. Graz, **2001**, 57.

5- Summary

By reaction of sodium/potassium phosphanide with 1,2-dichlorotetramethyldisilane, anionic ring compounds with Si-P arrangements such as $[P_2Si_4Me_8]^{2-}$ and $[P_3Si_5Me_{10}]^-$ could be obtained.

$[P_3Si_5Me_{10}]^-$ was formed by reacting $P(Na/K)_3$ with 1,25 eq. of 1,2-dichlorotetramethyldisilane. The compound was stable but the reaction could not be successfully reproduced.

$[P_2Si_4Me_8]^{2-}$ was obtained by adding 0,5 eq. of 1,2-dichlorotetramethyldisilane to the suspension of $P(Na/K)_3$. The ring was stable and could be used for further reactions.

Reactions of sodium/potassium phosphanide with other chlorosilanes such as Cl_2SiMe_2, Ph_2SiCl_2 and $Cl_2MeSiSi(SiMe_3)_3$ were performed with the expectation to isolate different ring and cage-like compounds. A mixture of products was obtained and no pure compounds could be isolated.

To study the reactivity of $[P_2Si_4Me_8]^{2-}$ and $[P_3Si_5Me_{10}]^-$ successfully obtained, some reactions were performed.

Attempts to bridge $[P_3Si_5Me_{10}]^-$ and obtain the cages $P_6Si_{11}Me_{22}$ and $P_6Si_{12}Me_{24}$ by reacting with Cl_2SiMe_2 and $(ClSiMe_2)_2$ in a molar ratio of 1:2 respectively did not work. The protonation of $[P_3Si_5Me_{10}]^-$ with trifluoroacetic acid gave the cage $P_3Si_5Me_{10}H$, which displays two possible conformations in the solution.

The reaction of $[P_2Si_4Me_8]^{2-}$ with $(Me_3Si)_3SiCl$ led to the formation of the ring $P_2Si_{12}Me_{14}$ consisting of two hypersilyl groups attached to the two P atoms of the dianion. A crystal structure of the ring was obtained.
Other chlorosilanes such as $SiCl_4$, $(SiMe_2Cl)_2$, $(Cl_2MeSi)_2$, Si_2Cl_6, $Cl_2Si_3Me_6$ and $Cl_2MeSiSi(SiMe_3)_3$ were added to the dianion $[P_2Si_4Me_8]^{2-}$, but no pure reaction products could be isolated.

In order to obtain a P-Sn-P atom arrangement, tin dichloride was added to the dianion. The reaction didn't work , but reacting the dianion with Ph_2SnCl_2 led to the formation of the cage $P_2Si_4Me_8SnPh_2$. The crystal structure of the cage was obtained.

P-P-P bonds were formed in the reaction of $[P_2Si_4Me_8]^{2-}$ with Cl_2PPh and $(CH_3)_3CPCl_2$, as deduced from the ^{31}P-NMR spectra. No crystal structures could be obtained to confirm the formation of the cages.

The cages $P_2Si_4Me_8GePh_2$ and $P_2Si_4Me_8Ge$ could not be obtained. P-Ge-P bonds were not formed.