



Phosphanes with bulky oligosilyl substituents

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ARTICLE INFO

Article history:

Received 31 October 2008

Received in revised form 28 November 2008

Accepted 2 December 2008

Available online 10 December 2008

Keywords:

Silylphosphanes

X-ray diffraction

NMR spectroscopy

ABSTRACT

By reaction of dichloroheptasilane $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiCl}_2$ with lithiumphosphanides LiPHR , the silylphosphanes $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiClPHR}$ with $\text{R} = 2, 4, 6\text{-tri-}tert\text{-butylphenyl}$ (= supermesityl, Mes^*) (**1**) and $\text{Si}(\text{SiMe}_3)_3$ (= hypersilyl, Hyp) (**2**) were prepared. Both compounds were characterized with X-ray diffraction, multinuclear NMR spectroscopy and elemental analysis. Compound **1** did not react with $n\text{-BuLi}$, but only with a large excess of $tert\text{-BuLi}$. Phosphasilene $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{Si}=\text{PMe}^*$ could be identified by a ^{31}P NMR signal at +346 ppm. All attempts to separate it from the reaction mixture failed due to many by-products which had formed through SiSi and SiP bond cleavage. Lithiation of **2** was possible with 4.2 equiv. of $tert\text{-BuLi}$, and crystals of the lithiumphosphanide $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiClPLiHyp}$ (**3**) could be obtained from THF, albeit in a quality not sufficient for X-ray diffraction. All attempts to achieve LiCl elimination and formation of the phosphasilene $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{Si}=\text{PSi}(\text{SiMe}_3)_3$ failed due to the unusual stability of the lithiumphosphanide. Prolonged refluxing in toluene (110 °C) only led to complete loss of coordinated THF, and $^{31}\text{P}/^{7}\text{Li}$ spin spin coupling could be observed in the ^{31}P NMR spectrum ($^1J_{\text{PLi}} = 84$ Hz).

Reaction of potassium phosphanide $[(\text{SiMe}_3)_3\text{Si}]\text{SiMe}_3\text{PK}$ with SiCl_4 led to the formation of $[(\text{SiMe}_3)_3\text{Si}]\text{Si}(\text{SiMe}_3)\text{P}(\text{SiCl}_3)$ (**4**), which could be successfully characterized with X-ray diffraction and multinuclear NMR spectroscopy. SiP bond lengths vary between 218 pm (SiCl_3) and 230 pm (hypersilyl). Despite these differences, $^{31}\text{P}^{29}\text{Si}$ coupling constants are nearly identical (92.4 Hz and 85.5 Hz, respectively).

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1. Introduction

It is well known that contrary to the classic double bond rule, multiple bonds between third row elements can be kinetically stabilized with large organic groups. For instance, the synthesis of the first isolable disilene $\text{R}_2\text{Si}=\text{SiR}_2$ bearing four mesityl groups R was reported in 1981, and a combination of mesityl and supermesityl groups (supermesityl = $\text{Mes}^* = 2,4,6\text{-tri-}tert\text{-butylphenyl}$) was used to stabilize the phosphasilene $\text{Mes}_2\text{Si}=\text{PMes}^*$ [1,2]. Subsequently it was shown that other substituents such as $tert\text{-butyl}$ or $\text{CH}(\text{SiMe}_3)_2$ and even silyl groups may serve the same purpose.

Ab initio calculations for model systems bearing SiH_3 substituents indicate a stabilizing electronic effect of silyl groups, which for larger SiR_3 is superimposed by steric effects. For instance, the SiSi bond strength in disilenes measured by the $\text{Si}=\text{Si}$ stretching force constant increases smoothly in the series $\text{H}_2\text{Si}=\text{SiH}_2$, $(\text{SiH}_3)\text{H-Si}=\text{SiH}(\text{SiH}_3)$ and $(\text{SiH}_3)_2\text{Si}=\text{Si}(\text{SiH}_3)_2$, which can be explained with π -electron delocalisation into antibonding $\sigma^*(\text{SiH})$ orbitals [3]. Moreover, the $\text{Si}_2\text{Si}=\text{SiSi}_2$ backbone is planar. Opposite to that, SiSi stretching force constants in disilanes decrease with increasing number of silyl substituents.

Recently, the synthesis of the first isolable disilyne has been described, which is also stabilized by two bulky silyl substituents of

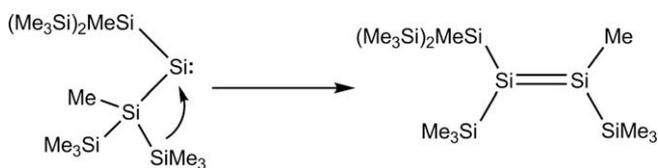
the type $\text{Si}^i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]_2$ [4]. We therefore asked ourselves the question whether bulky oligosilyl groups containing SiSi single bonds (such as $\text{Si}(\text{SiMe}_3)_3$) might also be capable to stabilize double or triple bonds of third row elements. These are substituents even less electronegative than SiH_3 or SiMe_3 , and interactions with antibonding $\sigma^*(\text{SiSi})$ orbitals supposedly exert a stabilizing effect on the π -electron system. The steric demand of the oligosilyl group can be increased further by substituting some methyl groups with larger organic substituents such as ^iPr or ^tBu . Moreover, as SiSi bonds are much more reactive than CC or SiC, they might offer the possibility to perform reactions in the substituent sphere, without affecting the double bond. For instance, SiMe_3 -groups in oligosilyl substituents such as $\text{Si}(\text{SiMe}_3)_3$ can be cleaved with KO^tBu at temperatures as low as -70 °C, giving an anionic silicon center $\text{SiK}(\text{SiMe}_3)_2$ and $\text{Me}_3\text{SiO}^t\text{Bu}$ [5].

However, the use of oligosilyl groups poses some severe synthetic difficulties, such as facile migration of silyl groups. Di(oligosilyl)silylenes which normally form disilenes by dimerization undergo very rapid silyl migration, rearranging into disilenes as shown in Scheme 1.

For this reason, we were unable to obtain $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{Si}=\text{Si}[\text{SiMe}(\text{SiMe}_3)_2]_2$ from silylene $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{Si}$ by dimerization. Instead, various cyclotrisilanes were obtained formed through silyl migration and addition of silylenes to disilenes [6]. So far, only a handful of disilenes substituted with oligosilyl groups have been described in the literature, among them a fused bicyclic system as

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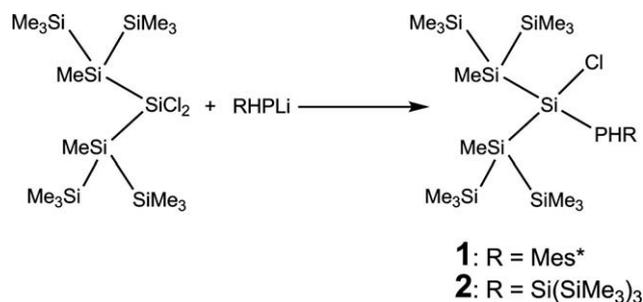


Scheme 1. Silylene to disilene rearrangement of (oligosilyl)silylenes.

well as disilenes with Si=SiH or Si=SiCl bonds which contain Si-Me(Si^tBu₃)₂ or SiH(Si^tBu₃)₂ groups [7–9]. They were prepared by reduction of a 1,2-dihalodisilane, and not by dimerization of a silylene.

A further problem with the use of oligosilyl groups stems from the ease of SiSi bond cleavage during reductive dehalogenation, which normally is used to form silylenes or disilenes from halogenated precursors. The number of by-products may be quite considerable, which certainly does not facilitate isolation of pure compounds. Noteworthy, silyl migration does not occur with oligosilylphosphinidenes such as (SiMe₃)₃SiP. (SiMe₃)₃SiP=PSi(SiMe₃)₃ is formed quickly by dimerization, which is the only di(oligosilyl) diphosphene described in the literature [10].

A fair number of silicon–phosphorus double bonded systems have been described so far, which also include some P-silylated derivatives, albeit none with oligosilyl groups [11]. Up to now, the best method for the synthesis of phosphasilenes is the thermal abstraction of a lithium halide LiX from phosphanido-halosilanes



Scheme 2. Synthesis of (chloro)oligosilylphosphanes **1** and **2**.

RPLi – SiXR₂ (preferably with X = F), a strategy which is also suitable for the preparation of arsenilenes. In this publication, we describe the preparation of the title phospho-halosilanes **1** and **2**, their lithiation with *tert*-BuLi and the subsequent attempts to achieve thermal LiX elimination.

2. Results and discussion

2.1. Synthesis of **1** and **2**

Previously reported dichloroheptasilane [(SiMe₃)₂MeSi]₂SiCl₂ and the lithium phosphanides RHPLi with R = 2,4,6-tri-*tert*-butylphenyl and Si(SiMe₃)₃ (further denoted as Mes* and hypersilyl, respectively) were used to prepare the highly congested chlorosilylphosphanes R₂SiCl – PHR as shown in **Scheme 2** (R' = (SiMe₃)₂MeSi; R = Mes* (**1**) or hypersilyl (**2**)).

Both phosphanes could be crystallized successfully from *n*-hexane, and X-ray structural data could be obtained. In **Fig. 1**, the molecular structures are shown with the help of ORTEP plots (30% probabilities), and selected interatomic distances and angles are given.

Due to steric interactions of the substituents, SiSi bonds are on the average 0.02–0.03 Å longer than considered as normal (2.32–2.35 Å; for instance 2.338 ± 0.004 Å in dodecamethylcyclohexasilane Si₆Me₁₂). With 2.28 Å, the PSi(1)–bond in **1** is 0.035 Å longer than in **2** (PSi(1) = 2.245 Å), which can be attributed to the increased steric demand of Mes* compared with hypersilyl. In **2**, the PSi(8) bond is longer than PSi(1) by about 0.04 Å, a difference which is also reflected in differing ¹J_{PSi} coupling constants which are 80 Hz for PSi(8) and 108 Hz for PSi(1). The steric congestion is also clearly reflected in some unusual bond angles. For instance, the angle Si(1)P(1)Si(8) is widened up to almost 121° in **2**, and Si(2)Si(1)Si(5) angles are also near this value (118.7° and 118.3°, respectively).

2.2. Lithiation of **1**

Compound **1** did not react with *n*-butyl-lithium even when the lithiation was tried in a non-polar solvent and at elevated temperatures. Just decomposition of *n*-BuLi was observed. With MeLi, only substitution of chlorine with methyl occurred, and

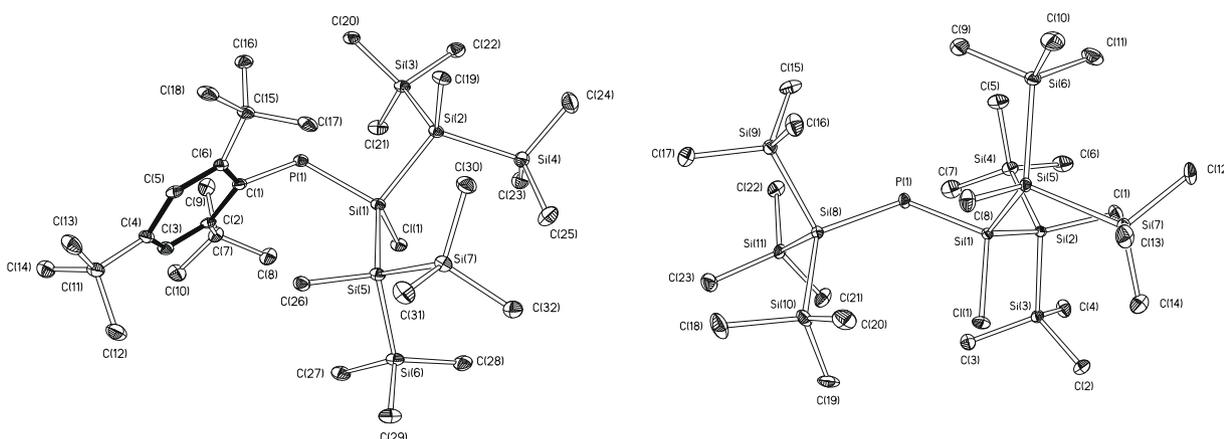


Fig. 1. ORTEP plots (30% probabilities) of the molecular structures of [(SiMe₃)₂MeSi]₂SiCl–PHMes* (**1**, left) and [(SiMe₃)₂MeSi]₂SiCl–PH[Si(SiMe₃)₃] (**2**, right). Selected interatomic distances and angles are as follows (Å and °): [(SiMe₃)₂MeSi]₂SiCl–PHMes* : P(1)Si(1): 2.2844(14); P(1)C(1): 1.856(4); Si(1)Cl(1): 2.1245(13); Si(1)Si(2): 2.3696(15); Si(1)Si(5): 2.3839(15); Si(2)Si(3): 2.3640(15); Si(2)Si(4): 2.3516(16); Si(5)Si(6): 2.3532(15); Si(5)Si(7): 2.3589(15); C(1)P(1)Si(1): 113.22(12); Si(2)Si(1)P(1): 97.89(5); Si(5)Si(1)P(1): 103.43(5); Si(2)Si(1)Si(5): 118.74(5); Si(4)Si(3)Si(2): 104.02(13); Si(6)Si(5)Si(7): 107.87(5); [(SiMe₃)₂MeSi]₂SiCl–PH[Si(SiMe₃)₃] : P(1)Si(1): 2.245(2); P(1)Si(8): 2.285(2); Cl(1)Si(1): 2.120(2); Si(1)Si(5): 2.346(2); Si(1)Si(2): 2.359(2); Si(2)Si(3): 2.350(2); Si(2)Si(4): 2.357(3); Si(5)Si(6): 2.351(2); Si(5)Si(7): 2.365(2); Si(8)Si(9): 2.351(2); Si(8)Si(10): 2.362(3); Si(8)Si(11): 2.364(2); Si(1)P(1)Si(8): 120.70(9); Cl(1)Si(1)P(1): 111.92(9); P(1)Si(1)Si(2): 101.28(9); P(1)Si(1)Si(5): 115.16(9); P(1)Si(8)Si(9): 103.68(9); P(1)Si(8)Si(10): 122.38(10); P(1)Si(8)Si(11): 99.82(9); Si(2)Si(1)Si(5): 118.3(9); Si(3)Si(2)Si(4): 110.61(9); Si(6)Si(5)Si(7): 109.94(9); Si(11)Si(8)Si(9): 107.75(9); Si(11)Si(8)Si(10): 108.15(9); Si(9)Si(8)Si(10): 113.57(10).

$[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiMe-PHMe}_3^*$ could be identified as the sole product with NMR spectroscopy ($\delta^{31}\text{P} = -110.9$ ppm, d, $^1J_{\text{PH}} = 226$ Hz; $\delta^{29}\text{Si} = -74.3$ ppm (bs, $\text{Si}(\text{SiMe}_3)_2\text{Me}$); $\delta^{29}\text{Si} = -10.5$ (d, SiMe_3 , $^3J_{\text{PSi}} = 4$ Hz); $\delta^{29}\text{Si} = -9.7$ (d, SiMe_3 , $^3J_{\text{PSi}} = \approx 1$ Hz); $\delta^{29}\text{Si} = -25.1$ (d, SiMe_2 , $^1J_{\text{PSi}} = 69$ Hz)). The lithiation of **1** was only possible with *tert*-butyl-lithium, but not without serious side reactions. When one equivalent of *tert*-BuLi was added, the predominant ^{31}P resonance was from the starting material **1**. A small doublet observed at -145.8 ppm ($^2J_{\text{PH}} = 31$ Hz) probably belonged to $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiH-PLiMe}_3^*$ formed through reduction of the SiCl bond with LiH, which is a decomposition product of lithiumalkyls. A singlet observed downfield at $+346.3$ ppm ($^1J_{\text{PSi}} = 161$ Hz) was from the phosphasilene $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{Si}=\text{PMe}_3^*$ formed by LiCl elimination from $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiCl-PLiMe}_3^*$. More *tert*-BuLi was added until the resonance of the starting silylphosphane **1** had disappeared completely. After exchange of the ether solvent with hexane followed by decantation from the salts, all attempts to obtain crystals of the phosphasilene failed due to very low yields. Even the identification of the phosphasilene by ^{29}Si NMR spectroscopy was not successful due to the same reasons.

When $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiF}_2$ was reacted with one equivalent of LiHPMe_3^* under the reaction conditions applied for the synthesis of **1**, only the signals of $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiF}_2$ could be detected in the ^{29}Si NMR spectrum. After replacement of the solvent with *n*-hexane and refluxing overnight, the ^{31}P NMR spectrum showed that LiHPMe_3^* had completely decomposed and that only a small part had reacted with the difluorosilane under concomitant LiF elimination ($\delta^{31}\text{P} = +350.2$ ppm, $^1J_{\text{PSi}} = 161$ Hz). Due to the very low yield, neither ^{29}Si resonances of the phosphasilene $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{Si}=\text{PMe}_3^*$ could be observed nor could crystals be obtained.

2.3. Lithiation of **2** to form **3**

The lithiation of **2** with *tert*-BuLi in THF at -78 °C gave a completely different outcome. 4.2 equiv. of the lithiating agent were necessary until the ^{31}P signal of starting **2** had disappeared. Side reactions involving SiP and SiSi bond cleavage also occurred. After reducing the volume of the solvent, light-orange crystals of $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiCl-PLiHyp}$ (**3**) precipitated, albeit not in a quality sufficient for X-ray analysis. The crystals were dissolved in THF and warmed up to 50 °C, but no LiCl elimination could be achieved. Consequently, THF was replaced with toluene and the solution was refluxed for 15 h at 110 °C. Again, no LiCl elimination was ob-

served. Instead, the extended reflux only led to total loss of coordinated THF, and splitting of the ^{31}P NMR signal into a quartet due to $^{31}\text{P}^7\text{Li}$ coupling could clearly be observed ($^1J_{\text{PLi}} = 84$ Hz). NMR data for **3** have been summarized in Section 3. Most certainly, the unusual resistance to LiCl elimination is caused by the less polar (and increased covalent) character of the LiP-bond due to the electron donating capability of both the hypersilyl and the Si_7 substituent. Treating **3** with MgBr_2 resulted in complete decomposition of the phosphanide, no phosphasilene could be detected spectroscopically.

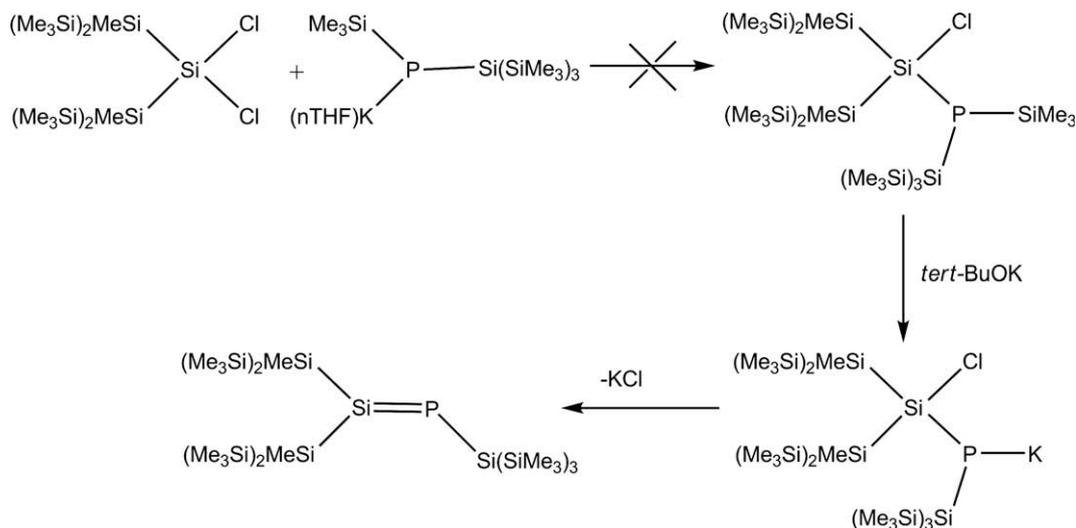
In a recent publication we have shown that *tert*-BuOK can be used to selectively cleave SiMe_3 -groups from trimethylsilylphosphanes under formation of potassium phosphanides and *tert*-butyl-trimethylsilyl ether. For instance, $\text{HypP}(\text{SiMe}_3)_2$ reacts quantitatively with formation of $\text{HypP}(\text{SiMe}_3)\text{K}$, and the hypersilyl group is not attacked under the reactions conditions (THF at -78 °C). We therefore attempted to prepare $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiCl-P}(\text{SiMe}_3)\text{Hyp}$ and to treat it with *tert*-BuOK to form $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiCl-PKHyp}$ as shown in Scheme 3.

It turned out that no reaction between $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiCl}_2$ and $\text{HypP}(\text{SiMe}_3)\text{K}$ could be achieved even at elevated temperatures of 50 – 60 °C, certainly due to steric strain the additional trimethylsilyl group introduces. In contrast, much smaller $\text{KP}(\text{SiMe}_3)_2$ did react quite readily forming $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiCl-P}(\text{SiMe}_3)_2$ in good yields. It is also noteworthy that phosphasilene $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{Si}=\text{PHyp}$ could not be prepared by salt elimination from $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiCl}_2$ and Li_2PHyp .

2.4. Synthesis of **4**

To explore further reactions of $\text{HypP}(\text{SiMe}_3)\text{K}$ with chlorosilanes, we reacted it with SiCl_4 in an attempt to prepare dichlorodiphosphanyl silane $\text{Hyp}(\text{SiMe}_3)\text{P-SiCl}_2\text{-P}(\text{SiMe}_3)\text{Hyp}$ as a potential precursor for $\text{HypKP-SiCl}_2\text{-PKHyp}$. It turned out that no disubstitution of SiCl_4 could be achieved due to steric reasons. Instead, $\text{Hyp}(\text{SiMe}_3)\text{P}(\text{SiCl}_3)$ formed in good yields, a phosphane bearing three different silyl groups. Crystals of **4** with a quality sufficient for X-ray analysis could be obtained from *n*-hexane. The molecular structure is presented in Fig. 2.

Chiral **4** possesses three different silyl substituents. Consequently, the SiP bonds $\text{Si}(1)\text{P}(1)$, $\text{Si}(2)\text{P}(1)$ and $\text{Si}(3)\text{P}(1)$ (SiCl_3 -group, SiMe_3 -group and hypersilyl group, respectively) differ in their bond length which increases from 2.185 Å (SiCl_3) to 2.289 Å



Scheme 3. Attempted reaction between $[(\text{SiMe}_3)_2\text{MeSi}]_2\text{SiCl}_2$ and $\text{HypP}(\text{SiMe}_3)\text{K}$.

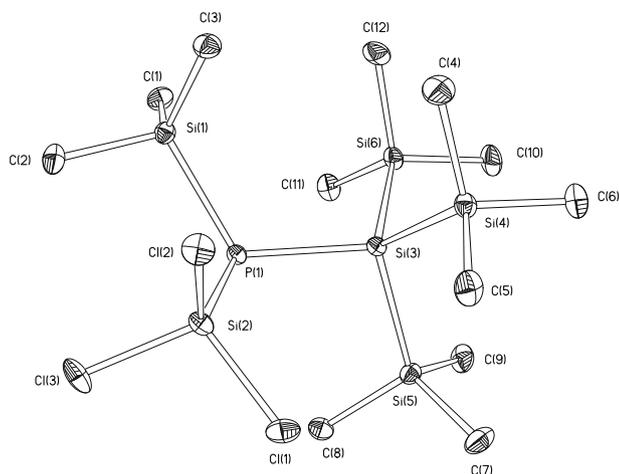


Fig. 2. ORTEP plot (30% probabilities) of the molecular structure of $(\text{SiMe}_3)(\text{SiCl}_3)\text{-PHyp}$ (**4**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$) are: P(1)Si(1): 2.2890(1); P(1)Si(2): 2.1850(7); P(1)Si(3): 2.3002(8); Si(2)Cl(1): 2.0413(7); Si(2)Cl(2): 2.0533(7); Si(2)Cl(3): 2.0421(9); Si(3)Si(4): 2.3676(10); Si(3)Si(5): 2.3820(8); Si(3)Si(6): 2.3656(8); Si(1)P(1)Si(3): 117.09(3); Si(1)P(1)Si(2): 100.81(2); Si(2)P(1)Si(3): 105.70(2); P(1)Si(3)Si(4): 121.23(3); P(1)Si(3)Si(5): 102.60(3); P(1)Si(3)Si(6): 103.05(2); P(1)Si(2)Cl(1): 112.15(3); P(1)Si(2)Cl(2): 116.91(3); P(1)Si(2)Cl(3): 111.28(3).

(SiMe_3) and to 2.300 Å (hypersilyl), mirroring the decreasing electronegativity of the substituents on the silicon atom ($\text{Cl} \rightarrow \text{Me} \rightarrow \text{SiMe}_3$). This can be understood using the concept of isovalent hybridisation which states that bonds to electronegative substituents (such as Cl) have more p-orbital character and that the remaining bonds therefore are characterized by an increased s-orbital contribution. Bond strengths usually increase with growing s-orbital character, and bond lengths decrease.

Quite obviously, the corresponding $^1J_{\text{P}^1\text{Si}}$ coupling constants which are 92.4 Hz (SiCl_3), 34.8 Hz (SiMe_3) and 85.5 Hz (hypersilyl) do not correlate with substituent electronegativities and bond

lengths. Ab initio calculations of coupling constants for the series H_2PSiR_3 with $\text{R} = \text{SiH}_3, \text{Me}, \text{H}, \text{Cl}$ and F indicate that $^1J_{\text{P}^1\text{Si}}$ is negative for all substituents, and that the strength of the bond (expressed with the harmonic SiP stretching force constant) increases with increasing electronegativity [12]. The calculations also predict quite similar coupling constants for the groups SiCl_3 (calc.: -57.2 , exp.: 52.2 Hz [13]) and $\text{Si}(\text{SiH}_3)_3$ (calc.: -50.2 Hz, exp.: 46.7 Hz for $\text{H}_2\text{PSi}(\text{SiMe}_3)_3$ [14]).

3. Experimental

3.1. General, NMR spectroscopy

As all compounds are air-sensitive, reactions were carried out either in an inert N_2 or Ar atmosphere using standard Schlenk techniques, or in a nitrogen filled glove box MBRAUN Unilab, supplied by M. Braun GmbH. All solvents were dried prior to use using a column solvent purification system and were then distilled under a N_2 atmosphere to remove all traces of oxygen. NMR spectra were recorded on a Varian INOVA 300 spectrometer (^1H : 299.95 MHz, ^{13}C : 75.43 MHz, ^{29}Si : 59.59 MHz, ^{31}P : 121.42 MHz). Shift are reported in ppm downfield from TMS (^1H , ^{29}Si , ^{13}C) and H_3PO_4 (^{31}P).

3.2. X-ray diffraction

For X-ray structure analyses, the crystals were mounted onto the tip of glass fibers and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation (0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT [15] and SADABS [16], respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97) [17]. 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. Diagrams were drawn with 30% probability thermal ellipsoids and all hydrogen atoms were

Table 1
Crystal data for **1**, **2** and **4**.

	$\text{C}_{32}\text{H}_{72}\text{ClPSi}_7$	$\text{C}_{23}\text{H}_{70}\text{ClPSi}_{11}$	$\text{C}_{12}\text{H}_{36}\text{Cl}_3\text{PSi}_6$
Empirical formula	$\text{C}_{32}\text{H}_{72}\text{ClPSi}_7$	$\text{C}_{23}\text{H}_{70}\text{ClPSi}_{11}$	$\text{C}_{12}\text{H}_{36}\text{Cl}_3\text{PSi}_6$
Formula weight	719.95	722.20	486.27
T [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, P2(1)/c	monoclinic, P2(1)/c	monoclinic, P2(1)/c
Unit cell dimension			
a [Å]	21.897(4)	17.861(4)	17.076(3)
b [Å]	12.699(3)	9.6358(19)	10.304(2)
c [Å]	16.325(3)	26.830(5)	15.971(3)
α ($^\circ$)	90	90	90
β ($^\circ$)	90.92(3)	95.11(3)	107.62(3)
γ ($^\circ$)	90	90	90
V [Å ³]	4538.9(16)	4599.3(16)	2678.1(9)
Z, D_{calc} [Mg/m ³]	4, 1.054	4, 1.043	4, 1.206
Absorption coefficient [mm ⁻¹]	0.324	0.418	0.667
F(000)	1576	1576	1032
Crystal size [mm]	0.44 × 0.30 × 0.24	0.40 × 0.20 × 0.15	0.52 × 0.42 × 0.30
θ Range for data collection [$^\circ$]	1.85–25.00	1.52–24.00	2.34–26.37
Limiting indices	$-26 < h < 26$, $-15 < k < 15$, $-19 < l < 19$	$-20 < h < 20$, $-11 < k < 11$, $-30 < l < 30$	$-21 < h < 21$, $-12 < k < 12$, $-19 < l < 19$
Reflections collected/unique (R_{int})	31 651/7963 (0.1055)	29 404/7211 (0.0727)	20 737/5460 (0.0406)
Completeness to θ max (%)	99.7	99.9	99.7
Absorption correction			
Max. and min. transmission	0.9264 and 0.8707	0.9400 and 0.8506	0.8250 and 0.7231
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7963/0/397	7211/0/352	5460/0/211
Goodness of Fit on I^2	0.969	1.412	1.062
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0636$, $wR_2 = 0.1375$	$R_1 = 0.0972$, $wR_2 = 0.1669$	$R_1 = 0.0295$, $wR_2 = 0.0738$
R indices (all data)	$R_1 = 0.0957$, $wR_2 = 0.1481$	$R_1 = 0.1091$, $wR_2 = 0.1714$	$R_1 = 0.0358$, $wR_2 = 0.0763$
Largest difference in peak and hole [$e \text{ \AA}^{-3}$]	0.833 and -0.395	0.508 and -0.419	0.604 and -0.233

omitted for clarity. Unfortunately, the obtained crystal quality for **1** and **2** was poor. This fact is reflected by quite high *R* and low theta values. Crystal and structure refinement data for **1–3** are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structures of compounds **1–3** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 703084 (**1**), 703085 (**2**) and 703083 (**3**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: internat. + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

3.3. Syntheses

3.3.1. Synthesis of 2,4,6-tri-*tert*-butylphenyl-(3-chloro-1,1,1,2,4,5,5,5-octamethyl-2,4-bis(trimethylsilyl)-*n*-pentasilanyl)phosphane (**1**)

A diethyl ether solution of 2,4,6-tri-*tert*-butylphenylphosphanide (1.14 g, 4.0 mmol) was added dropwise into a diethyl ether solution of 3,3-dichloro-1,1,1,2,4,5,5,5-octamethyl-2,4-bis(trimethylsilyl)-*n*-pentasilane (1.91 g, 4.0 mmol) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was then allowed to warm slowly to room temperature and was stirred overnight to complete the reaction. Diethyl ether was then removed by evaporation under reduced pressure and the reddish, oily residue was suspended in *n*-hexane. After filtration of the insoluble lithium salts, **1** crystallized at $-80\text{ }^{\circ}\text{C}$ in the form of colourless crystals suitable for single crystal X-ray analysis. The yield was 0.31 g (11%).

Anal. Calc. for $\text{C}_{32}\text{H}_{72}\text{Si}_7\text{PCl}$ (719.94 g/mol): C, 53.39, H, 10.08. Found: C, 53.35, H, 10.59%.

^1H NMR (C_6D_6): $\delta = 0.18$ (SiCH₃, 6H), $\delta = 0.32$ (s, Si(CH₃)₃, 18H), $\delta = 0.36$ (s, Si(CH₃)₃, 18H), $\delta = 1.31$ (9H, *tert*-Bu), $\delta = 1.70$ (18H, *tert*-Bu), $\delta = 5.18$ (d, PH, 1H, $^1J_{\text{PH}} = 226$ Hz), $\delta = 7.48$ (d, ArH, 2H, $^4J_{\text{PH}} = 2.4$ Hz).

^{29}Si NMR (C_6D_6): $\delta = -64.4$ (s, Si(SiMe₃)₂Me, $^2J_{\text{SiP}} < 1.0$ Hz), $\delta = -10.7$ (d, SiMe₃, $^3J_{\text{SiP}} = 4$ Hz), $\delta = -10.0$ (d, SiMe₃, $^3J_{\text{SiP}} = 2$ Hz), $\delta = 28.4$ (d, SiCl, $^1J_{\text{SiP}} = 92$ Hz).

^{31}P NMR (C_6D_6): $\delta = -92.5$ (d, $^1J_{\text{PH}} = 226$ Hz).

3.3.2. Synthesis of hypersilyl-(3-chloro-1,1,1,2,4,5,5,5-octamethyl-2,4-bis(trimethylsilyl)-*n*-pentasilanyl)phosphane (**2**)

A THF solution of lithium tris(trimethylsilyl)silylphosphanide (2.06 g, 7.2 mmol) was added dropwise to a solution of 3,3-dichloro-1,1,1,2,4,5,5,5-octamethyl-2,4-bis(trimethylsilyl)-*n*-pentasilane in THF at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was then allowed to warm to room temperature slowly and was stirred for another 12 h. THF was then removed by evaporation under reduced pressure. The reddish, oily residue was suspended in *n*-hexane, and the insoluble lithium salts were separated by decantation. At $-80\text{ }^{\circ}\text{C}$, **2** crystallized in form of colourless crystals which, after a second recrystallization were suitable for X-ray single crystal analysis. The yield was 1.75 g (37%).

Anal. Calc. for $\text{C}_{23}\text{H}_{70}\text{Si}_{11}\text{PCl}$ (722.21 g/mol): C, 38.25; H, 9.77. Found: C, 38.27; H, 9.76%.

^1H NMR (C_6D_6): $\delta = 0.36$ (s, 36H), $\delta = 0.41$ (s, 27H), $\delta = 0.49$ (s, 6H), $\delta = 2.05$ (d, 1H, $^1J_{\text{PH}} = 198$ Hz).

^{29}Si NMR (C_6D_6): $\delta = 29.8$ (d, SiCl, $^1J_{\text{SiP}} = 108$ Hz, $^2J_{\text{SiH}} = 6$ Hz), $\delta = -9.5$ (d, Si(Si(CH₃)₃)₃, $^2J_{\text{SiP}} = 10.0$ Hz), $\delta = -11.2$ (d, Si(CH₃)₃, $^3J_{\text{SiP}} = 1.0$ Hz), $\delta = -11.5$ (d, Si(CH₃)₃, $^3J_{\text{SiP}} = 6.0$ Hz), $\delta = -67.3$ (d, Si(SiMe₃)₂Me, $^2J_{\text{SiP}} = 12$ Hz), $\delta = -90.2$ (d, Si(SiMe₃)₃Me, $^1J_{\text{SiP}} = 80.0$ Hz).

^{31}P NMR (C_6D_6): $\delta = -210.1$ (d, $^1J_{\text{PH}} = 198$ Hz).

3.3.3. Synthesis of lithium hypersilyl-(3-chloro-1,1,1,2,4,5,5,5-octamethyl-2,4-bis(trimethylsilyl)-*n*-pentasilanyl)phosphanide (**3**)

Five milliliters of a 1.0 M *n*-pentane solution of *n*-butyl-lithium (0.50 mmol) was added to a solution of 0.09 g (0.12 mmol) of **2** in

THF at $-78\text{ }^{\circ}\text{C}$. The colour immediately turned yellow. The reaction mixture was then allowed to warm to room temperature slowly, and the completion was checked with ^{29}Si , ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Light-orange crystals of **3** precipitated from the THF solution at room temperature, but the quality of the crystals was not sufficient for X-ray diffraction. When an equimolar amount of *n*-butyl-lithium was used, the formation of the lithium phosphanide **3** could hardly be observed.

No LiCl elimination was observed upon warming the THF solution of **3** to $50\text{ }^{\circ}\text{C}$ over several hours. The solvent therefore was replaced by toluene, and the solution was refluxed for 15 h. Again, no LiCl elimination was observed. The extended reflux only led to a total removal of coordinated THF, which resulted in the splitting of the $^{31}\text{P}\{^1\text{H}\}$ signal into a 1:1:1:1 quartet due to $^{31}\text{P}^7\text{Li}$ coupling ($^1J_{\text{PLi}} = 84$ Hz).

^{31}P NMR (ppm, THF solution): $\delta = -339.9$.

^{29}Si NMR (ppm, THF solution): $\delta = -6.4$ (d, SiCl, $^1J_{\text{SiP}} = 114$ Hz), $\delta = -11.8$ (m, SiMe₃), $\delta = -12.5$ (s, SiMe₃), $\delta = -14.5$ (d, (SiMe₃)₃Si), $^2J_{\text{SiP}} = 16$ Hz), $\delta = -84.4$ (d, Si(SiMe₃)₂Me, $^2J_{\text{SiP}} = 33$ Hz), $\delta = -95.1$ (d, Si(SiMe₃)₃, $^1J_{\text{SiP}} = 166$ Hz).

3.3.4. Synthesis of hypersilyl(trichlorosilyl)trimethylsilylphosphane (**4**)

A diethyl ether solution of potassium (trimethylsilyl)-[tris(trimethylsilyl)silyl]phosphanide **3** (3.91 g, 10.0 mmol) was added dropwise to a diethyl ether solution of tetrachlorosilane (8.50 g, 5.0 mmol) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was then allowed to warm to room temperature slowly and was stirred overnight for completion. Diethyl ether was then removed by evaporation under reduced pressure, and the oily residue was suspended in *n*-hexane. After filtration of the insoluble potassium salts, **4** crystallized from *n*-hexane at $-80\text{ }^{\circ}\text{C}$. The quality of the colourless crystals was sufficient for a single crystal X-ray analysis. The yield was 2.10 g (43%). No disubstitution of SiCl₄ was observed.

Anal. Calc. for $\text{C}_{12}\text{H}_{36}\text{Si}_6\text{P}_2\text{Cl}_3$ (486.26 g/mol): C, 29.64; H, 7.46. Found: C, 28.74; H, 7.96%.

^1H NMR (ppm, C_6D_6): $\delta = 0.34$ (s, Si[Si(CH₃)₃]₃, 27H), $\delta = 0.44$ (d, Si(CH₃)₃, 9H).

^{13}C NMR (ppm, C_6D_6): $\delta = -3.4$ (d, Si[Si(CH₃)₃]₃, $^3J_{\text{PC}} = 2.3$ Hz), $\delta = 4.7$ (d, Si(CH₃)₃, $^2J_{\text{PC}} = 12.2$ Hz).

^{29}Si NMR (ppm, C_6D_6): $\delta = -89.4$ (d, Si(SiMe₃)₃, $^1J_{\text{SiP}} = 85.8$ Hz), $\delta = -9.4$ (d, Si(SiMe₃)₃, $^2J_{\text{SiP}} = 9.1$ Hz), $\delta = 6.7$ (d, SiMe₃, $^1J_{\text{SiP}} = 34.8$ Hz), $\delta = 12.7$ (d, SiCl₃, $^1J_{\text{SiP}} = 92.4$ Hz).

^{31}P NMR (ppm, C_6D_6): $\delta = -206.9$.

4. Supplementary material

CCDC 703084, 703085 and 703083 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

The authors gratefully acknowledge financial support by the 'Fonds zur Förderung der wissenschaftlichen Forschung', FWF, Vienna (Project P-18176-N11).

References

- [1] R. West, M. Fink, J. Michl, *Science* 214 (1981) 1343.
- [2] C.N. Smit, F.M. Lock, F. Bickelhaupt, *Tetrahedron Lett.* 25 (1984) 3011.
- [3] M. Flock, private communication.
- [4] R. Kinjo, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* 129 (2007) 26.
- [5] C. Marschner, *Eur. J. Inorg. Chem.* 2 (1998) 221.
- [6] A. Dzambasky, J. Baumgartner, K. Hassler, *Silicon Chem.* 3 (2008) 271.
- [7] H. Kobayashi, T. Iwamoto, M. Kira, *J. Am. Chem. Soc.* 127 (2005) 15376.

- [8] N. Wiberg, W. Niedermayer, H. Nöth, M. Warchhold, *Z. Anorg. Allg. Chem.* 627 (2001) 1717.
- [9] N. Wiberg, W. Niedermayer, G. Fischer, H. Nöth, M. Suter, *Eur. J. Inorg. Chem.* (2002) 1066.
- [10] V. Cappello, J. Baumgartner, M. Flock, A. Dransfeld, K. Hassler, *Eur. J. Inorg. Chem.* (2006) 2393.
- [11] For a recent review see: M. Driess, *Coord. Chem. Rev.* 145 (1995) 1.
- [12] U. Laky, M. Flock, K. Hassler, in preparation.
- [13] M. Driess, C. Monse, K. Merz, *Z. Anorg. Allg. Chem.* 627 (2001) 1225.
- [14] V. Cappello, J. Baumgartner, A. Dransfeld, K. Hassler, *Eur. J. Inorg. Chem.* (2006) 4589.
- [15] SAINTPLUS: Software Reference Manual, Version 6.45; Bruker-AXS, Madison, WI, 1997–2003.
- [16] R.H. Blessing, *Acta Crystallogr. A* 51 (1995) 33; SADABS, Version 2.1; Bruker AXS: Madison, WI, 1998.
- [17] G.M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis (Release 97-2), Universität Göttingen, Göttingen, Germany, 1998.