

Novel silicon and phosphorus containing heterocycles [☆]

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Abstract

The reactions of two or three equivalents of lithium phosphinomethanides with di- or trifunctional chlorosilanes yield novel five- and six-membered heterocycles with silicon and phosphorus ring members by multistep rearrangements and/or transmetallation reactions. Silaethene intermediates are likely to be involved. Three different types of reactions are described.

(1) RSiCl_3 (a, R = Ph; b, R = Me; c, R = ^tBu) reacts with three equivalents of $\text{Li}[\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)]$ to give five-membered heterocycles $(\text{R})[(\text{Me}_3\text{Si})\text{C}(\text{PMe}_2)_2]\text{Si}-\text{C}(\text{SiMe}_3)=\text{PMe}_2-\text{PMe}-\text{CH}_2$, **11**, which are fluxional in solution. A PMe_2 group shift and transmetallation reaction are involved in their formation.

(2) PhSiCl_3 reacts with $\{\text{Li}[\text{C}(\text{PMe}_2)(\text{SiMe}_3)]\}_2 \times \text{TMEDA}$ to give a five-membered heterocycle $(\text{Ph})(\text{Me})\text{Si}-\text{C}(\text{SiMe}_3)_2-\text{SiMe}_2-\text{PMe}_2=\text{C}(\text{SiMe}_3)$, **17**, via an intermediate mono- and disubstitution product. This reaction involves ligand rearrangement, elimination of Me_2PCl , and an, Me_3Si and Me group shift within a silaethene framework.

(3) Ph_2SiCl_2 reacts with two equivalents of $\text{Li}[\text{CH}(\text{PMe}_2)_2]$ to give a six-membered heterocycle $[\text{Ph}_2\text{Si}-\text{C}(\text{PMe}_2)=\text{PMe}_2-]_2$, **18**, by transmetallation and LiCl elimination, possibly via a silaethene intermediate.

X-ray analyses of **11a**, **17** and **18** confirm the proposed molecular structures based on nuclear magnetic resonance spectroscopy.

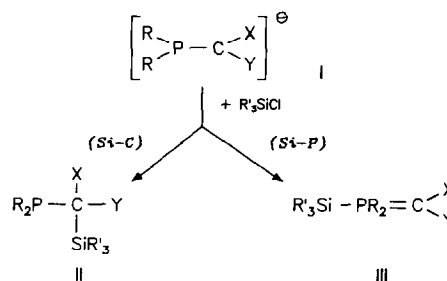
Keywords: Silicon; Phosphorus; Phosphinomethanides; Crystal structure; Silaheterocycles

1. Introduction

The ambidentate nature of phosphinomethanides I (Scheme 1) is well documented: they may react with electrophiles either via the phosphorus or the carbon atom. Si–C or Si–P bonds are formed with chlorosilanes. Thus, heteroelement substituted methanes II or phosphorus ylides III are obtained, depending on the nature of P and C substituents R, X and Y of the phosphinomethanide, as well as on the chlorosilane substituents R' and on the specific reaction conditions [1].

Some of the ylides are fluxional in solution. Furthermore, rearrangements of the products are often observed. As an example, PhSiCl_3 reacts with

$\text{Li}[\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)]$, **1**, to give a fluxional, pentacoordinate compound **2** under Si–P bond formation in high yield, which slowly rearranges (several weeks at ambient temperature) to the tetraheteroatom substituted methane derivative **3** (Si–C bond formation) and further to the ylide **4** involving a P–P bond formation (Scheme 2). An analogous ylide $\text{Me}_2\text{P}-\text{PMe}_2=\text{C}(\text{SiMe}_3)-(\text{SiCl}_2^t\text{Bu})$, **5**, is obtained from ^tBuSiCl₃ and **1** instantaneously.

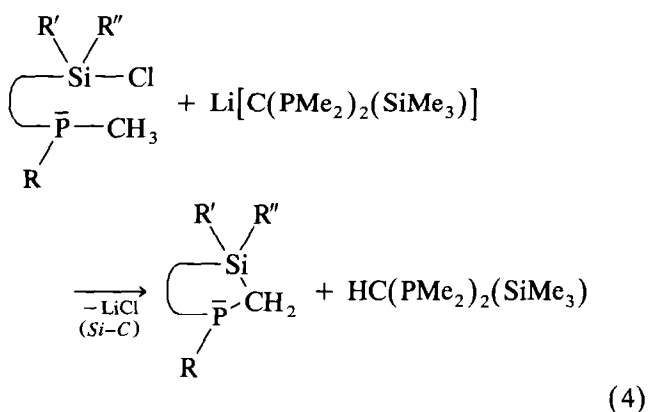
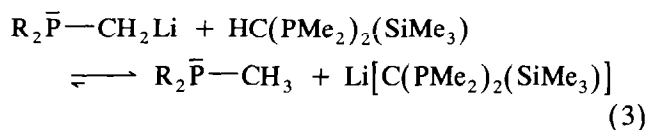


Scheme 1. Reaction of phosphinomethanides with chlorosilanes: Si–C and/or Si–P bond formation

[☆] Dedicated to Professor Dr. H. Schumann on the occasion of his 60th birthday.

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be formed analogously to **10a**. The final step in all three cases then results from transmetalation of **10a–10c** with **1**. Although this process is unusual in the sense that generally the stability of carbanions increases with an increasing number of heteroatoms, it may be explained by a shift of equilibrium (3) due to irreversible Si–C bond formation (Eq. (4)) [4].



The $^{31}\text{P}\{^1\text{H}\}$ nuclear magnetic resonance (NMR) spectra of **11a** and **11c** reveal the presence of two isomers (due to the relative orientation of the $\text{P}_\text{D}\text{Me}$ group) in an approximately 2:1 ratio. At -60°C two ABCD-type patterns are observed. Shift and coupling constants are within the expected range with the exception of $\delta(\text{P}_\text{A})$. Its unusual down-field shift obviously is

due to its incorporation into the five-membered ring. On warming, the signals of the exocyclic phosphorus nuclei P_B and P_C of both isomers broaden and, at $+60^\circ\text{C}$, a single signal for these two nuclei indicates a rapid exchange (Fig. 1), probably via a pentacoordinate silicon transition state. The NMR spectrum of **11b** is analogous to those of **11a** and **11c**, but only one isomer obviously is present (see Section 4). Since a reason for this discrepancy is not obvious, this point needs further investigations.

2.2. Molecular structure of **11a**

The structure of **11a** has been unambiguously established by X-ray crystallography of one of the isomers. Very air-sensitive, colourless crystals of one of the isomers of **11a** are obtained from pentane solution.

The solid state structure (Fig. 2, Table 1) reveals that the “free” PMe_2 group of the exocyclic diphosphinomethanide ligand adopts a rotational position enabling an approach to the silicon centre by a least-motion pathway. The corresponding Si1–P4 distance amounts to 3.708 Å, whereas Si–P3 (2.334(3) Å) reflects the presence of a normal single bond. The “ylidic” and “non-ylidic” P–C bonds of the monohapto bonded ligand are within the typical range (P3–C3, 1.717(7) Å; P4–C3, 1.778(7) Å).

The most important structural feature of **11a** is a novel type of five-membered heterocycle, which adopts an envelope conformation: P2 deviates by 0.588 Å from a plane through C2, Si1, C1, P1. The dihedral angle between this plane and the plane through P1, P2, C2

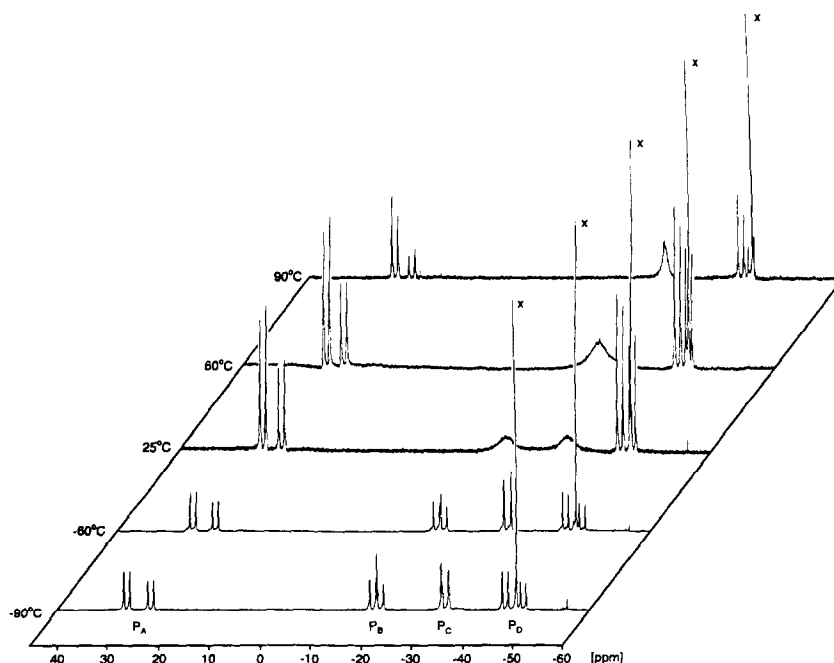


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra ($\text{C}_6\text{D}_5\text{CD}_3$) of **11a** at various temperatures (\times , $\text{HC}(\text{PMe}_2)_2(\text{SiMe}_3)$).

Table 1
Bond lengths (ångstroms) and angles (degrees) for **11a**

P(1)–C(1)	1.704(8)	P(1)–C(4)	1.788(9)
P(1)–C(5)	1.81(1)	P(1)–P(2)	2.195(4)
P(2)–C(6)	1.77(1)	P(2)–C(2)	1.863(8)
P(3)–C(3)	1.717(7)	P(3)–C(8)	1.812(7)
P(3)–C(7)	1.829(7)	P(3)–Si(1)	2.334(3)
P(4)–C(3)	1.778(7)	P(4)–C(9)	1.833(8)
P(4)–C(10)	1.841(8)	Si(1)–C(1)	1.807(7)
Si(1)–C(11)	1.876(8)	Si(1)–C(2)	1.906(8)
Si(2)–C(1)	1.833(8)	Si(2)–C(22)	1.876(9)
Si(2)–C(21)	1.88(1)	Si(2)–C(23)	1.881(9)
Si(3)–C(3)	1.825(7)	Si(3)–C(33)	1.87(1)
Si(3)–C(31)	1.86(1)	Si(3)–C(32)	1.89(1)
C(1)–P(1)–C(4)	116.6(4)	C(1)–P(1)–C(5)	116.4(5)
C(4)–P(1)–C(5)	104.6(6)	C(1)–P(1)–P(2)	111.0(3)
C(4)–P(1)–P(2)	107.2(4)	C(5)–P(1)–P(2)	99.2(5)
C(6)–P(2)–C(2)	98.6(6)	C(6)–P(2)–P(1)	95.2(5)
C(2)–P(2)–P(1)	90.4(3)	C(3)–P(3)–C(8)	111.7(4)
C(3)–P(3)–C(7)	114.4(3)	C(8)–P(3)–C(7)	101.5(4)
C(3)–P(3)–Si(1)	114.7(3)	C(8)–P(3)–Si(1)	104.3(3)
C(7)–P(3)–Si(1)	109.0(3)	C(3)–P(4)–C(9)	107.6(4)
C(3)–P(4)–C(10)	107.1(4)	C(9)–P(4)–C(10)	97.7(4)
C(1)–Si(1)–C(2)	113.8(3)	C(1)–Si(1)–C(2)	105.0(4)
C(11)–Si(1)–C(2)	112.0(4)	C(1)–Si(1)–P(3)	112.0(3)
C(11)–Si(1)–P(3)	110.2(2)	C(2)–Si(1)–P(3)	103.3(3)
P(1)–C(1)–Si(1)	109.7(4)	P(1)–C(1)–Si(2)	120.7(4)
Si(1)–C(1)–Si(2)	129.5(4)	P(2)–C(2)–Si(1)	115.9(4)
P(3)–C(3)–P(4)	107.9(4)	P(3)–C(3)–Si(3)	122.4(4)
P(4)–C(3)–Si(3)	127.3(4)		

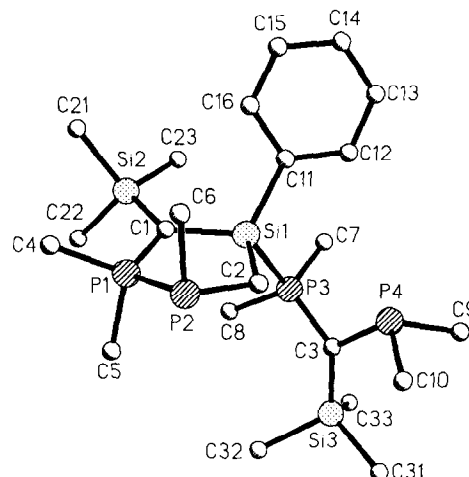


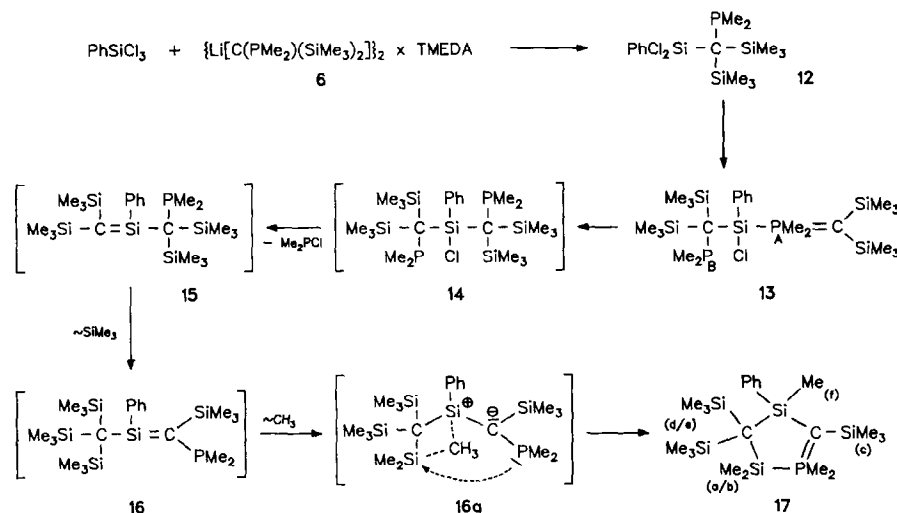
Fig. 2. Molecular structure of **11a** (H atoms omitted).

bond lengths: P2–C6 (1.77(1) Å) is unusually short, but a more profound discussion seems obsolete owing to disorder effects at this position. Nevertheless are the angles at P1 and P2 typical for tetra- and trivalent phosphorus respectively. The endocyclic angles may be understood as a consequence of the specific needs of a five-membered ring.

2.3. Reaction of PhSiCl_3 with $\{\text{Li}[\text{C}(\text{PMe}_2)(\text{SiMe}_3)_2]\}_2 \times \text{TMEDA}$, **6**

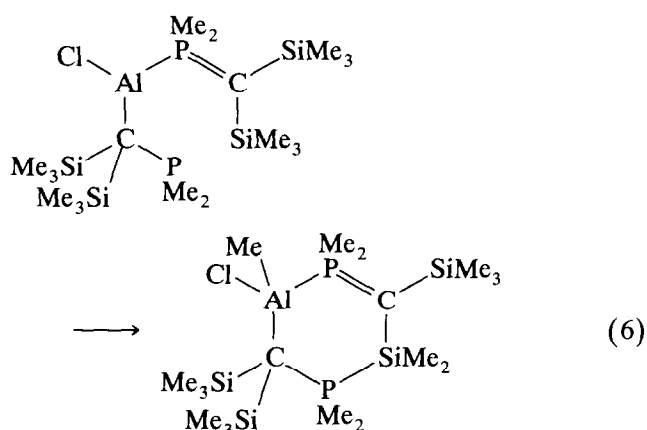
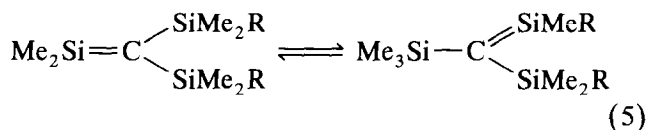
As in the reaction (Eq. (1)) of SiCl_4 and Me_2SiCl_2 with $\{\text{Li}[\text{C}(\text{PMe}_2)(\text{SiMe}_3)_2]\}_2 \times \text{TMEDA}$, **6**, mono- and disubstitution are also observed in the reaction of PhSiCl_3 with **6** (Scheme 4).

The analogous reaction sequence (monosubstitution, Si–C bond formation, **12**; disubstitution, Si–C and Si–P bond formation, **13**) is observed. **12** is isolated in an impure form from a 1:1 and **13** from a 1:2 reaction,



Scheme 4. Reaction of PhSiCl_3 with **6**: formation of **12** and **13** and subsequent rearrangement to **17**.

both as very air-sensitive colourless oils. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **13** exhibits an AB-type pattern, typical for this class of compounds. On storage of pure **13** at ambient temperature or at prolonged reaction times in solution, **13** is converted into the novel heterocycle **17**, which is obtained as very air-sensitive colourless crystals. No intermediates are detectable spectroscopically. For an explanation of this unusual rearrangement, the reaction pathway depicted in Scheme 4 seems reasonable. An isomerization **13** \rightarrow **14**, which is analogous to that in Scheme 2, initiates a multistep rearrangement: the sterically overcrowded **14** is not stable, release of steric strain is achieved by elimination of Me_2PCl , thus generating a silaethene derivative **15**. The fate of Me_2PCl is not clear: it cannot be detected spectroscopically. Although $\text{Me}_2\text{P}-\text{PMe}_2=\text{C}(\text{SiMe}_3)_2$ [**1a**] is identified in the mixture, which indicates a reaction of Me_2PCl with **6**, if starting from pure **13** this trapping reaction is not feasible, however. Likewise, **15** is not detected: it isomerizes by an SiMe_3 group migration to give **16**. This type of silaethene isomerization (probably an equilibrium) is unprecedented. It is followed by a methyl migration, which is reminiscent of a known type of equilibrium (see Eq. (5)) [5] and probably assisted by the influence of the neighbouring nucleophilic PMe_2 group. An Si–P bond formation with the unsaturated silicon atom thus generated completes the ring closure to give **17**. This last two steps are closely related to the formation of an aluminum heterocycle (Eq. (6)) described previously [6].



In line with the proposed structure of **17**, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the heterocycle reveal the presence of six different Si– CH_3 groups. The single line $^{31}\text{P}\{^1\text{H}\}$ NMR resonance at $\delta(\text{P}) = -25.45$ is accompanied by two sets of satellites (27.1 and 89.9 Hz), which are mirrored in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum and thus give convincing evidence for the proposed struc-

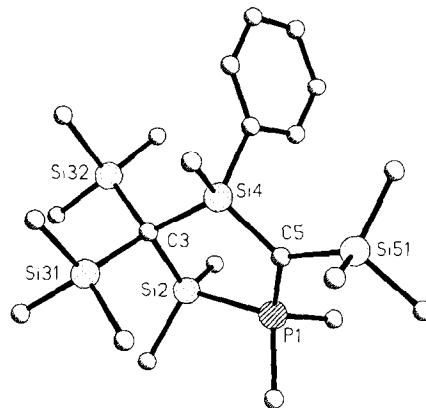


Fig. 3. Molecular structure of **17** (H atoms omitted).

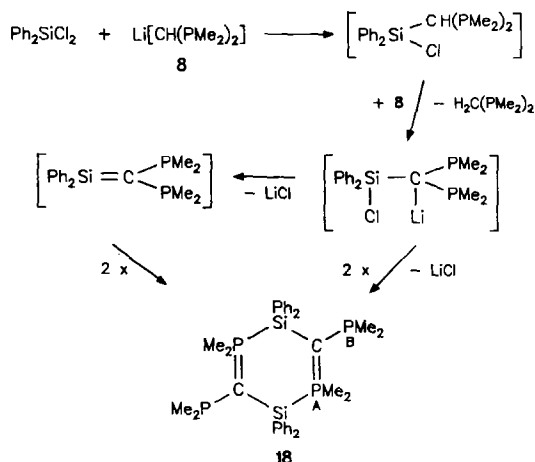
ture. The structure unambiguously has been confirmed by an X-ray analysis.

2.4. Molecule Structure of **17**

The dominant structural feature of **17** is the presence of a novel type of five-membered heterocycle with four atoms (P1, Si2, Si4, C5) approximately lying within a plane with a maximum deviation at Si4 (-0.069 \AA), whereas the tetrahedral C3 atom deviates by 0.459 \AA from this plane (Fig. 3, Table 2). The ring is constituted by a phosphorus ylide moiety with a planar C5 atom, two tetrahedral silicon atoms and a carbon atom which is part of a tetrasilyl substituted methane moiety. The

Table 2
Bond lengths (ångstroms) and angles (degrees) for **17**

P(1)–C(5)	1.697(3)	P(1)–C(11)	1.833(3)
P(1)–C(12)	1.833(3)	P(1)–Si(2)	2.268(1)
Si(2)–C(21)	1.865(3)	Si(2)–C(22)	1.869(3)
Si(2)–C(3)	1.888(2)	Si(4)–C(5)	1.822(3)
Si(4)–C(41)	1.880(3)	Si(4)–C(42)	1.899(3)
Si(4)–C(3)	1.955(2)	Si(31)–C(313)	1.873(3)
Si(31)–C(312)	1.880(3)	Si(31)–C(311)	1.881(3)
Si(31)–C(3)	1.923(2)	Si(32)–C(322)	1.872(3)
Si(32)–C(323)	1.873(3)	Si(32)–C(321)	1.881(3)
Si(32)–C(3)	1.918(2)	Si(51)–C(511)	1.790(5)
Si(51)–C(5)	1.823(3)	Si(51)–C(512)	1.850(5)
Si(51)–C(513)	1.879(5)		
C(5)–P(1)–C(11)	116.7(2)	C(5)–P(1)–C(12)	116.8(2)
C(11)–P(1)–C(12)	99.7(2)	C(5)–P(1)–Si(2)	103.47(9)
C(11)–P(1)–Si(2)	107.7(1)	C(12)–P(1)–Si(2)	112.7(1)
C(21)–Si(2)–C(22)	104.5(2)	C(21)–Si(2)–C(3)	120.3(1)
C(22)–Si(2)–C(3)	116.7(1)	C(21)–Si(2)–P(1)	107.8(1)
C(22)–Si(2)–P(1)	104.4(1)	C(3)–Si(2)–P(1)	101.77(8)
C(5)–Si(4)–C(41)	111.0(1)	C(5)–Si(4)–C(42)	110.2(1)
C(41)–Si(4)–C(42)	102.8(1)	C(5)–Si(4)–C(3)	109.6(1)
C(41)–Si(4)–C(3)	112.4(1)	C(42)–Si(4)–C(3)	110.8(1)
Si(2)–C(3)–Si(32)	109.7(1)	Si(2)–C(3)–Si(31)	108.6(1)
Si(32)–C(3)–Si(31)	110.4(1)	Si(2)–C(3)–Si(4)	103.9(1)
Si(32)–C(3)–Si(4)	114.7(1)	Si(31)–C(3)–Si(4)	109.3(1)
P(1)–C(5)–Si(4)	114.3(1)	P(1)–C(5)–Si(51)	122.2(2)
Si(4)–C(5)–Si(51)	123.4(2)		

Scheme 5. Proposed pathway for the formation of **18**.

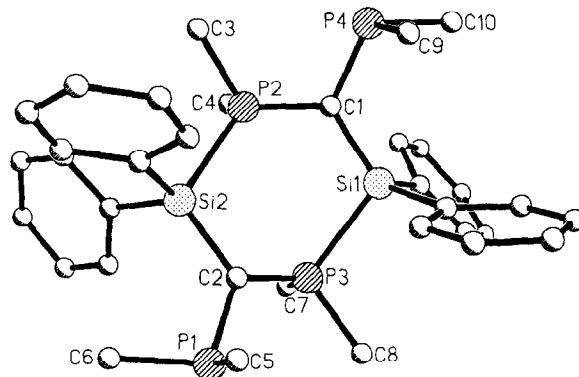
P1–C5 distance is in the typical range for phosphorus ylides (1.697(3) Å). The Si2–P1 distance (2.268(1) Å) is exceptionally short compared with acyclic counterparts (cf. Si–P in **7a**, **7b**: 2.367 Å [1b]), whereas Si4–C3 (1.955(2) Å) is very long, obviously for steric reasons. All other bond lengths and angles are within the expected range. Particularly important in the light of the unusual mode of formation of **17** is the presence of a methyl group at Si4 with a standard Si–C bond length (1.880(3) Å).

2.5. Reaction of Ph_2SiCl_2 with $\text{Li}[\text{CH}(\text{PMe}_2)_2]$, **8**

In contrast to the reaction of SiCl_4 with two equivalents of **8** (Eq. (2)), Ph_2SiCl_2 reacts with **8** under formation of a six-membered heterocycle **18** (Scheme 5).

Steric hindrance obviously renders a second substitution step more difficult than a transmetallation reaction. Diphosphinomethane, $\text{CH}_2(\text{PMe}_2)_2$, is eliminated and detected in the reaction mixture. A subsequent LiCl elimination occurs either intra- (yielding a silaethene derivative) or intermolecularly. Both possible ways, which cannot be distinguished, since no intermediates could be detected, finally would lead to the novel six-membered heterocycle **18**, which was isolated as very air-sensitive colourless crystals from toluene. Formally, in **18** two diphosphinocarbenes, $\text{C}(\text{PMe}_2)_2$, bridge two diphenyl silylenes via carbon and phosphorus atoms. A similar formal diphosphinocarbene formation from diphosphinomethanide ligand by transmetallation at a zirconocene metal centre obviously is closely related [7].

The NMR spectra of **18** are in full accord with the given structure. In particular, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reveals an AA'BB'-type pattern with the expected parameters. The structure of **18** unambiguously has been confirmed by an X-ray analysis.

Fig. 4. Molecular structure of **18** (H atoms omitted).

2.6. Molecular structure of **18**

In contrast to expectation, the solid state structure does not confirm the presence of a centrosymmetric molecule as may be expected from NMR spectroscopy, since toluene is incorporated into the lattice. Nevertheless, the main structural features are that of the expected six-membered ring with two Ph_2Si fragments connected via P-ylide bridges (Fig. 4, Table 3). The planar ylide carbon atoms C1 and C2 both are connected to exocyclic PMe_2 groups. All distances and angles are in the expected range. In particular, the endocyclic ylidic P–C distances (P2–C, 1.719(2) Å; P3–C2, 1.719(2) Å) and

Table 3
Bond lengths (ångstroms) and angles (degrees) for **18**

P(1)–C(2)	1.802(2)	P(1)–C(6)	1.829(3)
P(1)–C(5)	1.838(3)	P(2)–C(1)	1.719(2)
P(2)–C(3)	1.813(3)	P(2)–C(4)	1.826(3)
P(2)–Si(2)	2.313(1)	P(3)–C(2)	1.719(2)
P(3)–C(8)	1.814(2)	P(3)–C(7)	1.818(2)
P(3)–Si(1)	2.302(1)	P(4)–C(1)	1.803(2)
P(4)–C(10)	1.841(3)	P(4)–C(9)	1.847(3)
Si(1)–C(1)	1.795(2)	Si(1)–C(21)	1.877(3)
Si(1)–C(11)	1.887(2)	Si(2)–C(2)	1.800(2)
Si(2)–C(31)	1.882(2)	Si(2)–C(41)	1.882(2)
C(2)–P(1)–C(6)	104.9(1)	C(2)–P(1)–C(5)	103.8(1)
C(6)–P(1)–C(5)	97.6(1)	C(1)–P(2)–C(3)	111.7(1)
C(1)–P(2)–C(4)	115.3(1)	C(3)–P(2)–C(4)	100.8(1)
C(1)–P(2)–Si(2)	113.03(9)	C(3)–P(2)–Si(2)	105.84(9)
C(4)–P(2)–Si(2)	109.2(1)	C(2)–P(3)–C(8)	111.6(1)
C(2)–P(3)–C(7)	115.3(1)	C(8)–P(3)–C(7)	101.9(1)
C(2)–P(3)–Si(1)	112.60(8)	C(8)–P(3)–Si(1)	105.03(9)
C(7)–P(3)–Si(1)	109.53(9)	C(1)–P(4)–C(10)	104.7(1)
C(1)–P(4)–C(9)	105.1(1)	C(10)–P(4)–C(9)	97.0(2)
C(1)–Si(1)–C(21)	113.4(1)	C(1)–Si(1)–C(11)	116.3(1)
C(21)–Si(1)–C(11)	110.4(1)	C(1)–Si(1)–P(3)	110.22(8)
C(21)–Si(1)–P(3)	103.30(8)	C(11)–Si(1)–P(3)	101.73(8)
C(2)–Si(2)–C(31)	116.4(1)	C(2)–Si(2)–C(41)	115.3(1)
C(31)–Si(2)–C(41)	109.4(1)	C(2)–Si(2)–P(2)	110.47(8)
C(31)–Si(2)–P(2)	100.91(8)	C(41)–Si(2)–P(2)	102.50(8)
P(2)–C(1)–Si(1)	119.3(1)	P(2)–C(1)–P(4)	116.8(1)
Si(1)–C(1)–P(4)	123.6(1)	P(3)–C(2)–Si(2)	117.7(1)
P(3)–C(2)–P(1)	116.5(1)	Si(2)–C(2)–P(1)	124.0(1)

the exocyclic P–C distances (P4–C1, 1.803(2) Å; P1–C2, 1.802(2) Å) reflect the different nature of these bonds. Probably because of the steric effects, the ring slightly deviates from a boat conformation. Thus C3 and C8 enclose a dihedral angle of 7.1°.

3. Conclusion

Novel five- and six-membered heterocycles with endocyclic phosphorus and silicon atoms can be obtained from the reaction of chlorosilanes with two or more equivalents of lithium phosphinomethanides by multi-step rearrangement processes and/or transmetallation reactions. Silaethene intermediates are likely to be involved, but could not yet be detected. Further studies will be focused on the trapping and/or isolation of possible intermediates by varying the substitution pattern. Theoretical studies on the rearrangement pathway are in progress. Nevertheless, the herein reported results open a new, promising field for the synthesis of unprecedented phosphasilaheterocycles. Moreover, a new class of facile skeleton rearrangements simultaneously spotlights the fragile nature of heteroatom substituted methanes and ylides.

4. Experimental part

4.1. Preparation of compounds

All compounds were prepared and handled in dry nitrogen atmosphere by using conventional vacuum line techniques. Sodium–potassium alloys were employed for drying and storage of the solvents, which were redistilled immediately prior to their use. PhSiCl₃, MeSiCl₃, ^tBuSiCl₃ and Ph₂SiCl₂ were dried over K₂CO₃ and distilled prior to use. Li[C(PMe₂)₂(SiMe₃)], **1**, {Li[C(PMe₂)(SiMe₃)₂]}₂·x TMEDA, **6** and Li[CH(PMe₂)₂], **8**, were synthesized according to literature [8]. Instrumentation, spectroscopy and elemental analysis were as described previously [1].

4.1.1. Preparation of (R)[(SiMe₃)C(PMe₂)₂][Si–C(SiMe₃)=PMe₂–PMe–CH₂] **11** (a, R = Ph; b, R = Me; c, R = ^tBu)

1.52 g (7.10 mmol) of **1** were dissolved in 30 ml of diethyl ether at –100°C (in the case of **11c**, –78°C). To this suspension 0.34 ml (2.13 mmol) of PhSiCl₃, 0.25 ml (2.13 mmol) of MeSiCl₃ or 0.41 g (2.13 mmol) of ^tBuSiCl₃, dissolved in 20 ml of diethyl ether, were added dropwise during a period of 1 h. The yellowish reaction mixture was allowed to warm up to room temperature and stirred for 12 h. The solvent was

replaced by 20 ml of pentane and the LiCl precipitate was filtered off. Evaporation of the filtrate gave a yellow oil (in the case of **11b**, **11c**, yield not determined) which was identified by ³¹P {¹H} NMR spectroscopy as a mixture of HC(PMe₂)₂(SiMe₃) [8] and **11b** or **11c**. In the case of **11a**, colourless crystals were obtained together with a yellow oil, which was decanted, and the crystals were washed with cold pentane. A residual amount of HC(PMe₂)₂(SiMe₃), ca. 10%, remained with the crystal fraction. The yield and ³¹P NMR spectra relate to the unseparated oil–crystal mixture; the melting point, elemental analysis and ¹H, ¹³C NMR data relate to the crystal fraction (isomer 1).

11a

Yield, 1.64 g; melting point, 114°C. Anal. calcd. for C₂₂H₄₆P₄Si₃ (518.77): C, 50.97; H, 8.87; Cl, 0.00. Found: C, 48.47; H, 8.50; Cl, 0.00.

NMR (C₆D₅CD₃). ³¹P{¹H} (+60°C): *isomer 1*, δ(P) = 28.66 (dt, ¹J(P_AP_D) = 187.0, ³J(P_AP_{B/C}) = 8.6, P_A), –25.25 (br, P_{B/C}), –40.96 (dt, ¹J(P_AP_D) = 187.0, ³J(P_{B/C}P_D) = 8.6, P_D); *isomer 2* δ(P) = 25.16 (dt, ¹J(P_AP_D) = 189.1, ³J(P_AP_{B/C}) = 8.6, P_A), –25.25 (br, P_{B/C}), δ(P) = –43.16 (d, ¹J(P_AP_D) = 189.1, P_D). ³¹P{¹H} (–60°C). *isomer 1*, δ(P) = 30.52 (dd, ¹J(P_AP_D) = 182.7, ³J(P_AP_B) = 17.2, P_A), –17.73 (dd; ²J(P_BP_C) = 227.8, ³J(P_AP_B) = 17.2, P_B), –31.69 (dd; ²J(P_BP_C) = 227.8, ⁵J(P_CP_D) = 12.9, P_C), –43.36 (dd, ¹J(P_AP_D) = 182.7, ⁵J(P_CP_D) = 12.9, P_D); *isomer 2*, δ(P) = 26.12 (dd, ¹J(P_AP_D) = 184.8, ³J(P_AP_B) = 17.2, P_A), –19.12 (dd; ²J(P_BP_C) = 225.7, ³J(P_AP_B) = 17.2, P_B), –31.77 (d; ²J(P_BP_C) = 227.8, ⁵J(P_CP_D) = 12.9, P_C), –46.61 (dd, ¹J(P_AP_D) = 184.8, ⁵J(P_CP_D) = 10.7, P_D). ¹³C{¹H} (C₆D₆, +25°C) δ(C) = 140.62 (m, C₁), 135.74 (t, ³J(P_{B/C}C) = 3.8, C_{2/6}), 129.26 (s, C₄), 127.89 (s, C_{3/5}), 21.97 (br, d, ¹J(P_AC) = 24.8, P_AMe), 21.26 (br, d, ¹J(P_AC) = 25.3, P_AMe), 19.93 (br, P_{B/C}Me₂), 19.18 (br, P_{B/C}Me₂), 16.51 (br, d, ¹J(P_DC) = 39.7, P_DMe), 9.71 (dd, ¹J(P_DC) = 24.2, ²J(P_AC) = 3.3, P_DCH₂), 7.18 (t, ³J(P_{B/C}C) = 1.6, SiMe₃), 5.48 (d, ³J(P_AC) = 3.3, SiMe₃). ¹H (C₆D₆, +25°C): δ(H) = 8.09 (m, 2H, Ar), 7.25 (m, 3H, Ar), 1.44 (br, 6H, PMe₂), 1.43 (br, 6H, PMe₂), 1.17 (dd, ²J(PH) = 11.7, ³J(PH) = 9.3, 3H, PMe), 1.08 (dd, ²J(PH) = 4.4, ³J(PH) = 2.5, 3H, PMe), 0.94 (br, d, ²J(PH) = 11.7, 2H, PCH₂), 0.60 (dd, ²J(PH) = 15.1, ³J(PH) = 4.4, 3H, PMe), 0.47 (s, 9H, SiMe₃), 0.16 (s, 9H, SiMe₃).

MS (EI, 70 eV): *m/e* = 518 (M⁺, 0.6%), 503 (M⁺–CH₃, 0.3%), 457 (M⁺–PMe₂, 0.2%), 311 (M⁺–C(PMe₂)₂(SiMe₃), 15%).

Atomic parameters are collected in Table 4.

11b

Yield, 1.79 g. NMR (C₆D₆, +25°C). ³¹P{¹H} (+25°C). δ(P) = 26.90 (dt, ¹J(P_AP_D) = 185.9, ³J(P_AP_{B/C}) = 8.6, P_A), –18.38 (br, d, ²J(P_BP_C) =

Table 4

Atomic coordinates and equivalent isotropic displacement parameters for **11a** ($U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor)

	$10^4 x/a$	$10^4 y/b$	$10^4 z/c$	$U(\text{eq})$ ($\times 10^3 \text{ \AA}^2$)
P(1)	4281(3)	6421(1)	9782(1)	45(1)
P(2)	6125(3)	5758(1)	9765(2)	65(1)
P(3)	2444(2)	5837(1)	7153(1)	26(1)
P(4)	4360(2)	4899(1)	6757(1)	30(1)
Si(1)	4604(2)	6257(1)	7965(1)	31(1)
Si(2)	2957(3)	7421(1)	8668(1)	39(1)
Si(3)	674(3)	4680(1)	7172(2)	45(1)
C(1)	3941(9)	6727(3)	8787(5)	36(2)
C(2)	5590(1)	5635(4)	8589(5)	47(2)
C(3)	2487(8)	5110(3)	7131(4)	31(2)
C(4)	4860(1)	6885(4)	10666(6)	67(3)
C(5)	2650(2)	6005(7)	10158(8)	101(5)
C(6)	7750(2)	6232(6)	9677(9)	95(4)
C(7)	2217(9)	6171(3)	6084(4)	35(2)
C(8)	683(9)	6100(3)	7641(5)	41(2)
C(9)	3930(1)	4534(4)	5718(5)	52(2)
C(10)	5060(1)	4279(3)	7403(6)	44(2)
C(11)	6004(8)	6598(3)	7228(5)	36(2)
C(12)	6425(9)	6349(3)	6460(5)	37(2)
C(13)	7544(9)	6614(4)	5965(5)	43(2)
C(14)	8259(9)	7110(4)	6233(6)	46(2)
C(15)	7883(9)	7364(3)	6998(6)	46(2)
C(16)	6762(9)	7111(3)	7486(5)	42(2)
C(21)	4210(1)	8020(4)	9159(6)	64(3)
C(22)	1020(1)	7450(4)	9205(7)	65(3)
C(23)	2530(1)	7600(3)	7488(5)	46(2)
C(31)	1100(2)	3907(4)	7180(1)	107(5)
C(32)	-310(1)	4774(6)	8217(8)	85(4)
C(33)	-880(1)	4827(5)	6269(7)	74(3)

219.2, P_B), -34.24 (br, d, $^2J(P_B P_C) = 219.2, P_C$), -43.88 (dd, $^1J(P_A P_D) = 184.8, ^5J(P_C P_D) = 12.9, P_D$).

11c

Yield, 1.73g.

NMR ($C_6D_5CD_3$, $^{31}P\{^1H\}$ (+25°C): *isomer 1*, $\delta(P) = 26.26$ (dt, $^1J(P_A P_D) = 185.0, ^3J(P_A P_{B/C}) = 8.5, P_A$), -17.51 (br, d, $^2J(P_B P_C) = 190.2, P_B$), -38.23 (br, d, $^2J(P_B P_C) = 185.6, P_C$), -44.80 (d, $^1J(P_A P_D) = 183.7, P_D$); *isomer 2*, $\delta(P) = 23.65$ (dd, $^1J(P_A P_D) = 183.7, ^3J(P_A P_B) = 21.2, P_A$), -18.08 (dd, $^2J(P_B P_C) = 186.5, ^3J(P_A P_B) = 21.2, P_B$), -39.27 (d, $^2J(P_B P_C) = 187.9, P_C$), -49.52 (d, $^1J(P_A P_D) = 183.7, P_D$). $^{31}P\{^1H\}$ (-60°C): *isomer 1*, $\delta(P) = 26.50$ (dd, $^1J(P_A P_D) = 180.3, ^3J(P_A P_B) = 13.9, P_A$), -17.89 (dd, $^2J(P_B P_C) = 194.2, ^3J(P_A P_B) = 13.9, P_B$), -38.57 (d, $^2J(P_B P_C) = 194.2, P_C$), -45.44 (d, $^1J(P_A P_D) = 180.3, P_D$); *isomer 2*, $\delta(P) = 24.01$ (dd, $^1J(P_A P_D) = 180.4, ^3J(P_A P_B) = 23.2, P_A$), -19.11 (dd, $^2J(P_B P_C) = 176.3, ^3J(P_A P_B) = 23.1, P_B$), -40.57 (d, $^2J(P_B P_C) = 175.7, P_C$), -53.07 (d, $^1J(P_A P_D) = 180.3, P_D$).

4.1.2. Preparation of $PhSiCl_2[C(PMe_2)(SiMe_3)_2]_2$, **12**

A suspension of $\{Li[C(PMe_2)(SiMe_3)_2]\}_2 \cdot x$ TMEDA, **6** (1.03 g; 1.81 mmol) in 50 ml of diethyl ether was

cooled to -78°C . $PhSiCl_3$ (0.58 ml, 3.62 mmol) was added. After warming up to ambient temperature the mixture was stirred for 2 h. The solvent was replaced by 30 ml of pentane, and, after filtration, the pentane was removed in vacuo and a yellowish oil (0.67 g) was obtained, which, by NMR spectroscopy, was identified as a 1:1 mixture of **12** and **13** (see below).

NMR data (C_6D_6 , +25°C) for **12**. $^{31}P\{^1H\}$: $\delta(P) = -29.78$ (s). 1H : $\delta(H) = 8.23$ (br, 2H, Ar), 7.09 (br, 3H, Ar), 1.23 (d, $^2J(PH) = 5.9, 6H, PMe_2$), 0.29 (s, 18H, $SiMe_3$).

4.1.3. Preparation of $(PMe_2)(SiMe_3)_2C-Si(Ph)(Cl)-PMe_2=C(SiMe_3)_2$, **13**

To a suspension of $\{Li[C(PMe_2)(SiMe_3)_2]\}_2 \cdot x$ TMEDA, **6** (1.41 g; 2.48 mmol) in 50 ml of diethyl ether were added 0.40 ml (2.48 mmol) of $PhSiCl_3$ at -78°C . After warming up to ambient temperature under stirring the mixture was stirred for another 2 h. The solvent was replaced by 30 ml of pentane, and, after filtration, the pentane was removed in vacuo and a yellowish oil (1.39 g) was obtained.

NMR (C_6D_6 , +25°C). $^{31}P\{^1H\}$: $\delta(P) = -7.88$ (d, $^3J(P_A P_B) = 15.7, P_A$), -38.23 (d, $^3J(P_A P_B) = 15.7, P_B$). $^{29}Si\{^1H\}$: $\delta(Si) = 0.49$ (d; $^2J(P_B Si) = 5.2, SiMe_3$), -7.08 (d; $^2J(P_A Si) = 5.9, SiMe_3$). $^{13}C\{^1H\}$: $\delta(C) 138.38$ (dd; $^3J(P_A C) = 13.8, ^4J(P_B C) = 1.1, C_{2/6}$), 133.69 (dd, $^2J(P_A C) = 18.2, ^3J(P_B C) = 3.8, C_1$), 130.94 (s, C_4), 127.64 (s, $C_{3/5}$), 22.07 (dd, $^1J(P_A C) = 45.1, ^4J(P_B C) = 4.4, P_A Me$), 20.47 (dd, $^1J(P_A C) = 46.2, ^4J(P_B C) = 6.1, P_A Me$), 16.77 (d, $^1J(P_B C) = 16.6, P_B Me$), 15.20 (d, $^1J(P_B C) = 25.9, P_B Me$), 7.80 (br, $SiMe_3$), 7.49 (br, $SiMe_3$), 5.48 (br, $SiMe_3$), 5.43 (br, $SiMe_3$). 1H : $\delta(H) = 8.29$ (br, 2H, Ar), 7.11 (br, 3H, Ar), 1.60 (d, $^2J(PH) = 11.3, 3H, P_A Me$), 1.39 (d, $^2J(PH) = 13.2, 3H, P_A Me$), 1.38 (d, $^2J(PH) = 2.9, 3H, P_B Me$), 1.15 (d, $^2J(PH) = 3.9, 3H, P_B Me$), 0.49 (br, 9H, $SiMe_3$), 0.42 (s, 9H, $SiMe_3$), 0.20 (br, 9H, $SiMe_3$), 0.00 (s, 9H, $SiMe_3$).

4.1.4. Preparation of $(Ph)(Me)Si-C(SiMe_3)=PMe_2-SiMe_2-C(SiMe_3)_2$, **17**

Storage of a saturated solution of 1.39 g (2.40 mmol) of **17** at room temperature for two months results in the formation of colourless crystals. Removal of the volatiles in vacuo yielded pure **17** (1.14 g, 2.36 mmol, 98.3%) (melting point 136°C).

Anal. calcd. for $C_{22}H_{47}PSi_5$ (483.02): C, 54.71; H, 9.81; Si, 29.07. Found: C, 52.71; H, 10.08; Si, 29.63.

The formation of **17** from **13**, which obviously contained **6**, in $C_6D_5CD_3$ solution at $+60^\circ\text{C}$ was monitored. In this case, an AB spin system was identified as $Me_2P-PMe_2=C(SiMe_3)_2$ (1a). NMR data (C_6D_6 , +25°C) of **17** (the assignment of $SiCH_3$ signals is not unambiguous in all cases). $^{31}P\{^1H\}$: $\delta(P) = -25.45$ (s, S satellites: $^1J(PSi) = 89.9; ^2J(PSi) = 27.1$). $^{29}Si\{^1H\}$: $\delta(Si) = 8.45$ (d, $^2J(PSi) = 26.8, SiPhMe$), 7.37 (c

Table 5

Atomic coordinates and equivalent isotropic displacement parameters for **17** ($U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor)

	$10^4 x/a$	$10^4 y/b$	$10^4 z/c$	$U(\text{eq})$ ($\times 10^3 \text{ \AA}^2$)
P(1)	8239(1)	3097(1)	7082(1)	33(1)
Si(2)	7400(1)	3642(1)	8033(1)	29(1)
Si(4)	8980(1)	3824(1)	5717(1)	25(1)
Si(31)	10413(1)	4146(1)	8633(1)	33(1)
Si(32)	7249(1)	4520(1)	7092(1)	30(1)
Si(51)	9941(1)	2973(1)	4740(1)	39(1)
C(3)	8501(3)	4049(1)	7359(2)	24(1)
C(5)	9100(3)	3287(1)	5868(2)	30(1)
C(11)	6548(4)	2774(1)	6520(4)	54(1)
C(12)	9436(4)	2770(1)	8321(3)	52(1)
C(21)	7702(4)	3552(1)	9881(3)	48(1)
C(22)	5234(3)	3636(1)	7435(4)	47(1)
C(41)	10819(3)	4035(1)	5314(3)	40(1)
C(42)	7439(3)	3969(1)	4193(2)	30(1)
C(43)	7565(3)	4308(1)	3423(3)	35(1)
C(44)	6411(4)	4414(1)	2332(3)	44(1)
C(45)	5101(4)	4185(1)	1965(3)	50(1)
C(46)	4951(4)	3845(1)	2678(3)	52(1)
C(47)	6109(3)	3738(1)	3770(3)	41(1)
C(311)	10165(4)	4329(1)	10326(3)	54(1)
C(312)	11734(4)	4535(1)	8148(4)	52(1)
C(313)	11619(3)	3684(1)	8969(3)	44(1)
C(321)	6678(4)	4674(1)	8707(3)	53(1)
C(322)	8308(4)	4948(1)	6519(3)	49(1)
C(323)	5340(3)	4496(1)	5862(3)	41(1)
C(511)	9240(1)	3093(2)	3003(5)	201(5)
C(512)	12097(6)	2974(2)	5220(8)	153(3)
C(513)	9489(8)	2432(1)	4860(6)	123(2)

$^1J(\text{PSi}) = 88.5$, SiMe_2), 0.26 (d, $^3J(\text{PSi}) = 8.2$, SiMe_3), 0.10 (s, SiMe_3), -7.19 (d, $^2J(\text{PSi}) = 2.7$, SiMe_3). $^{13}\text{C}(\text{H})$: $\delta(\text{C}) = 146.75$ (d, $^3J(\text{PC}) = 2.2$, C_1), 136.08 (s, $\text{C}_{2/6}$), 128.40 (s, C_4), 127.38 (s, $\text{C}_{3/5}$), 20.06 (d; $^1J(\text{PC}) = 38.5$, PMe), 18.37 (d, $^1J(\text{PC}) = 36.9$, PMe), 8.11 (d; $^3J(\text{PC}) = 8.3$, SiMe-f), 7.75 (s, $\text{SiMe}_3\text{-e}$), 6.36 (s, $\text{SiMe}_3\text{-d}$), 5.15 (d; $^3J(\text{PC}) = 2.8$, $\text{SiMe}_3\text{-c}$), 3.70 (d, $^2J(\text{PC}) = 10.4$, SiMe-b), 3.23 (d, $^2J(\text{PC}) = 12.1$, SiMe-a). ^1H : $\delta(\text{H}) = 7.72$ (br, 2H, Ar), 7.17 (br, 3H, Ar), 1.11 (d, $^2J(\text{PH}) = 10.2$, 3H, PMe), 1.07 (d, $^2J(\text{PH}) = 10.8$, 3H, PMe), 0.32 (s, 9H, SiMe_3), 0.19 (s, 3H, SiMe), 0.16 (s, 3H, SiMe), 0.15 (s, 3H, SiMe), 0.12 (s, Si satellites: $^2J(\text{SiH}) = 5.3$, 9H, SiMe_3), -0.12 (s, 9H, SiMe_3).

MS (CI, 150 eV): $m/e = 482$ (M^+ , 100%), 467 ($\text{M}^+ - \text{CH}_3$, 37.5%), 409 ($\text{M}^+ - \text{SiMe}_3$, 13%).

Atomic parameters are collected in Table 5.

4.1.5. Preparation of $[\text{Ph}_2\text{Si}-\text{C}(\text{PMe}_2)=\text{PMe}_2]_2$, **18**

To a suspension of $\text{LiCH}(\text{PMe}_2)_2$, **8** (1.18 g, 8.31 mmol) in 30 ml of diethyl ether, 0.79 ml (3.74 mmol) of Ph_2SiCl_2 were added at -78°C . The mixture reacts spontaneously forming a colourless, viscous suspension. After warming up to room temperature a yellowish

suspension is formed, which is stirred for another 12 h. The solvent is replaced by pentane and, after filtration and evaporation of the pentane, a yellow oil (0.60 g), mainly consisting of $\text{H}_2\text{C}(\text{PMe}_2)_2$, remains. The solid residue of the pentane extraction is dissolved in toluene and, after filtration and evaporation of toluene, yellow crystals of **18** (1.49 g, 2.36 mmol, 63%), melting point, 183°C , are obtained.

Anal. calcd. for $\text{C}_{34}\text{H}_{44}\text{P}_4\text{Si}_2$ (632.79): C, 64.54; H, 7.00. Found: C, 62.16; H, 6.88.

NMR (C_6D_6 , $+25^\circ\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ (AA'BB' spin system); $\delta(\text{P}) = -24.15$ ($\text{P}_{\text{A/A}'}$), $\delta(\text{P}) = -38.37$ ($\text{P}_{\text{B/B}'}$), $J(\text{AA}') = J(\text{BB}') = 0.0$ Hz, $J(\text{AB}) = J(\text{A'B}') = 84.0$ Hz, $J(\text{AB}') = -J(\text{A'B}) = 8.7$, Hz. $^{13}\text{C}\{^1\text{H}\}$: $\delta(\text{C}) = 137.88$

Table 6

Atomic coordinates and equivalent isotropic displacement parameters for **18** ($U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor)

	$10^4 x/a$	$10^4 y/b$	$10^4 z/c$	$U(\text{eq})$ ($\times 10^3 \text{ \AA}^2$)
P(1)	-1327(1)	5593(1)	1082(1)	24(1)
P(2)	511(1)	2258(1)	2461(1)	20(1)
P(3)	-1205(1)	4933(1)	2346(1)	17(1)
P(4)	3502(1)	3887(1)	3402(1)	30(1)
Si(1)	815(1)	5120(1)	3130(1)	18(1)
Si(2)	-467(1)	2910(1)	1563(1)	17(1)
C(1)	1634(3)	3804(3)	2981(1)	22(1)
C(2)	-833(3)	4570(3)	1673(1)	20(1)
C(3)	1677(3)	1258(3)	2299(1)	33(1)
C(4)	-1131(3)	730(3)	2696(1)	35(1)
C(5)	634(4)	7011(4)	998(1)	43(1)
C(6)	-1802(3)	4345(3)	404(1)	32(1)
C(7)	-3125(3)	3620(3)	2482(1)	28(1)
C(8)	-1340(3)	6743(3)	2407(1)	28(1)
C(9)	5059(3)	5667(4)	3241(1)	40(1)
C(10)	3594(4)	4544(4)	4166(1)	43(1)
C(11)	-243(3)	4772(3)	3767(1)	21(1)
C(12)	-707(3)	3363(3)	3988(1)	28(1)
C(13)	-1639(3)	2995(3)	4410(1)	35(1)
C(14)	-2117(3)	4032(3)	4618(1)	35(1)
C(15)	-1656(3)	5449(3)	4414(1)	32(1)
C(16)	-728(3)	5815(3)	3994(1)	26(1)
C(21)	2285(3)	7168(3)	3192(1)	23(1)
C(22)	2885(3)	8152(3)	3715(1)	32(1)
C(23)	4074(4)	9621(3)	3743(2)	44(1)
C(24)	4678(4)	10129(3)	3251(2)	43(1)
C(25)	4102(3)	9189(3)	2728(1)	39(1)
C(26)	2923(3)	7730(3)	2699(1)	29(1)
C(31)	1164(3)	3131(3)	1159(1)	22(1)
C(32)	2714(3)	4245(3)	1383(1)	31(1)
C(33)	3970(3)	4375(4)	1118(2)	41(1)
C(34)	3715(4)	3419(4)	630(2)	45(1)
C(35)	2192(4)	2318(4)	394(1)	43(1)
C(36)	937(3)	2186(3)	657(1)	31(1)
C(41)	-2298(3)	1114(3)	1242(1)	22(1)
C(42)	-3810(3)	1115(3)	1148(1)	29(1)
C(43)	-5196(3)	-218(4)	954(1)	41(1)
C(44)	-5093(4)	-1573(3)	848(1)	43(1)
C(45)	-3616(3)	-1613(3)	933(1)	34(1)
C(46)	-2238(3)	-284(3)	1126(1)	28(1)

(m, C₁), 136.54 (d, ⁴J(PC) = 2.2, C_{2/6}), 129.73 (s, C₄), 127.83 (s, C_{3/5}), 19.03 (dd, ¹J(PC) = 17.1, ³J(PC) = 8.3, P_BMe₂), 17.10 (dd, ¹J(PC) = 38.5, ³J(PC) = 14.9, P_AMe₂). ¹H: δ(H) = 8.01 (br, 8H, Ar), 7.14 (br, 8H, Ar), 1.09 (“t”, N = 8.0, 24H, PMe₂).

Atomic parameters are collected in Table 6.

4.2. Crystal structure analysis of 11a, 17 and 18

Crystallographic measurements were made at 193 K (11a), 214 K (17), and 205 K (18) with graphite-mo-chromated Mo K_α radiation (λ = 0.71073 Å) on an ENRAF-NONIUS CAD4-Turbo diffractometer. The crystals used for measurement were colourless blocks of sizes 0.60 mm × 0.35 mm × 0.30 mm (11a), 0.50 mm × 0.35 mm × 0.25 mm (17), and 0.50 mm × 0.45 mm × 0.30 mm (18).

For each compound the unit-cell dimensions (Table 7) were determined by 100 reflections of high diffraction angles using values between θ = 9.22° and 11.98° (11a), θ = 9.17° and 12.02° (17), and θ = 8.24° and 12.21° (18). The intensity data were measured by continuous ω–θ (11a and 18) and ω (17) scans. Measured data were corrected for Lorentz and polarization effects [9]. For each compound, three standard reflections were

remeasured every hour during data collection. Of measured reflections only the reflections with F_o > 4σ(F_o), of which there were 4201 (11a), 4474 (17) and 5928 (18), were used in the structure analyses.

The structures were solved by direct methods [10]. Refinement was done by the full-matrix least-squares method. All calculations were performed using SHELXL-93 [11]. Empirical absorption correction was applied using DIFABS [12].

In the structural models all non-hydrogen atoms were assigned anisotropic displacement parameters. The coordinates of the hydrogen atoms were geometrically calculated and refined using the “riding model”.

Tables of H atom coordinates and thermal parameters and a complete list of bond length and angles have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen m.b.H., D-76344 Eggenstein-Leopoldshafen, under the following numbers: CSD 401666 (11a), CSD 401667 (18) and CSD 401668 (17).

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Table 7
Crystallographic data for 11a, 17 and 18

	11a	17	18
Molecular formula	C ₂₂ H ₄₆ P ₄ Si ₃	C ₂₂ H ₄₇ PSi ₅	C ₃₄ H ₄₅ P ₄ Si ₂ * 0.5C ₇ H ₈
Molecular mass (g mol ⁻¹)	418.74	483.02	675.92
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁ /c	P2 ₁ /n	P $\bar{1}$
d _{calc} (g cm ⁻³)	1.135	1.092	1.201
a (Å)	8.334(1)	8.753(1)	9.373(2)
b (Å)	23.600(2)	33.765(3)	9.687(2)
c (Å)	15.479(2)	10.155(1)	23.128(4)
α (deg)	90	90	91.01(1)
β (deg)	94.47(1)	101.79(1)	101.01(2)
γ (deg)	90	90	114.22(1)
V (Å ³)	3035(1)	2937.9(5)	1869.0(6)
Z	4	4	2
μ (mm ⁻¹)	0.376	0.305	0.291
Crystal dimensions (mm × mm × mm)	0.50 × 0.35 × 0.25	0.60 × 0.35 × 0.30	0.50 × 0.45 × 0.30
Data collection diffractometer	CAD4	CAD4	CAD4
Radiation	Mo K _α , graphite mono-chromator	Mo K _α , graphite mono-chromator	Mo K _α , graphite mono-chromator
2θ range (deg)	4–50	6–52	6–52
Reciprocal space	–9 ≤ h ≤ 9, 0 ≤ k ≤ 28, 0 ≤ l ≤ 18	–10 ≤ h ≤ 10, 0 ≤ k ≤ 41, 0 ≤ l ≤ 12	0 ≤ h ≤ 11, –11 ≤ k ≤ 10, –28 ≤ l ≤ 27
Scan mode	ω–θ	ω	ω–θ
Independent reflections	5325	5700	7283
Observed reflections	4201	4474	5928
Programs	SIR92, SHELXL-93	SIR92, SHELXL-93	SIR92, SHELXL-93
Parameters	270	267	419
R1 = Σ F _o – F _c / Σ F _o	0.1047	0.0423	0.0432
wR2 = {Σw(F _o – F _c) ² / Σw(F _o) ² } ^{1/2}	0.2460	0.1115	0.1096
Largest residual (e Å ⁻³)	4.341	1.054	0.557

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