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Some aspects of the chemistry of silylidene-phosphanes and -arsanes [1]

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Contents

Abstract

This paper summarizes some advances in the chemistry of silanylidene-phosphanes ("phosphasilenes", Si=P) and silanylidene-arsanes ("arsasilenes", Si=As) which have been achieved since 1991. The easy access to stable phospha- and arsa-silenes, having silyl groups attached to the

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[1] Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday.

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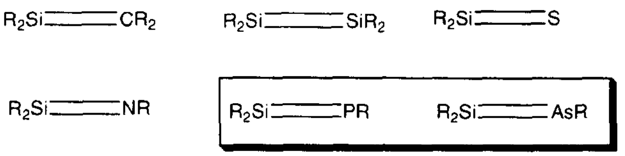
low-coordinate pnictogen atoms, has allowed the study of the molecular structures, NMR spectroscopic properties, and reactivity. It turned out that the structural and chemical features for phospha- and arsa-silenes are distinctly different to those observed for iminosilanes (Si=N).

Keywords: Silicon-phosphorus; Silicon-arsenic; Multiple bonds; Low-coordinate silicon

1. Introduction

Hardly a branch in main group chemistry was more explosively developed during the last ten years than that of compounds bearing low-coordinated heavy main group elements. Most of the efforts in this field were initiated and inspired by the astonishing developments in phosphorus and silicon chemistry. Spectacular breakthroughs include the syntheses of thermally resistant (stable) but nevertheless quite reactive alkylidene-phosphanes ("phospha-alkenes", P=C) [1], alkylidyne-phosphanes ("phospha-alkynes", P≡C) [2], phosphanylidene-phosphanes ("diphosphenes", P=P) [3], alkylidene-silanes ("silenes", Si=C) [4] and silylidene-silanes ("disilenes", Si=Si) [5]. The Si=Si bond is the weakest "double" bond possible in the element series C, N, O, Si, P, S [6], and is simply stabilized by sterically demanding organyl substituents attached to the heavy main group element. However, it proved more difficult to isolate stable compounds with Si=N (iminosilanes, "silane-imines") and Si=P bonds (silylidene-phosphanes, "phosphasilenes") (Scheme 1).

The synthesis of iminosilanes was first reported in the mid-1980s [7]. As a result of the difference in the spectroscopic electronegativity [8] of silicon (1.916) and nitrogen (3.066), the intrinsically more stable Si=N-π system compared with a Si=Si bond is extremely polarized and therefore dimerizes or polymerizes more readily. As in the case of alkylidene-silanes (Si=C), the high Lewis acidity of the low-coordinate silicon center predestined the formation of adducts with donor molecules such as LiF, THF, ketones [9], and therefore hampered the synthesis of "free" iminosilanes, proceeding via salt-elimination from suitable alkali metal–amido (halogensilanes). However, it has been shown that lithium–amido(fluorosilanes) may regarded as masked Si=N derivatives because they react like iminosilanes [10]. Although the Si=P bond is significantly less polar compared to a Si=N bond, which should provide a higher kinetic stability and, at the same time, less Lewis acidity on silicon, other difficulties appeared which have hampered the isolation of stable phosphasilenes (Si=P) [11]. For instance, it appeared that the Si=P bond is intrinsically less stable than the Si=N bond, and that steric protection on silicon is more important than on phosphorus.



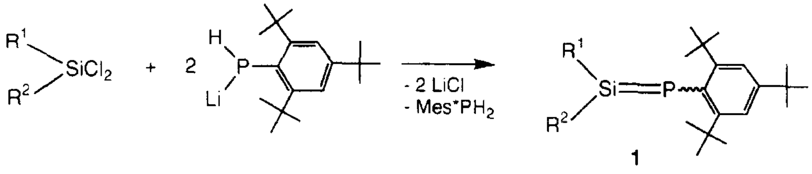
Scheme 1. Stable compounds to date containing λ^4,σ^3-coordinate silicon.

Up to now, the best method for the synthesis of stable and chemically activated phosphasilenes is achieved by thermal abstraction of LiF from suitable lithium-silylphosphanido-fluorosilanes [12]. Recently, it has been shown that this synthetic route, surprisingly, is also suitable for the preparation of silylidene-arsanes ("arsasilenes", As=Si) [13]. Thus it was possible to investigate the physical and chemical properties of Si=E bonds depending on the nature of the pnictogen atom E (E= N, P, As) [14].

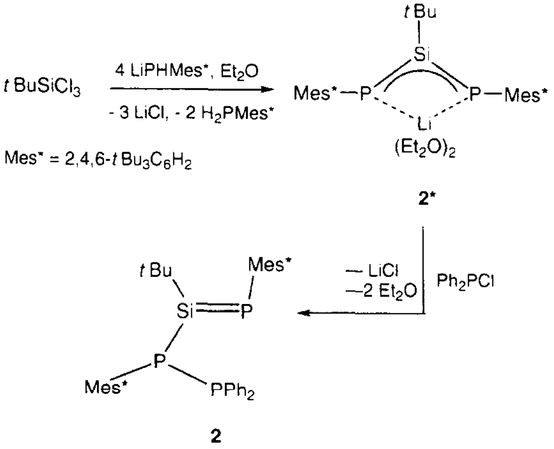
This review discusses the synthesis, spectroscopic and structural characterization and reactivity of stable silylidene-phosphanes and -arsanes.

2. Stable silylidene-phosphanes

The first moderately stable phosphasilene derivatives **1** were synthesized in 1984 (Eq. 1) [11]. They possess limited stability (up to 60 °C), and were characterized by NMR spectroscopy and chemical reactions.



Combination of the lithiumphosphanides RPHLi with suitable sterically demanding substituted dichlorosilanes R_2SiCl_2 in THF in a molar ratio of 2:1 resulted in the formation of **1** and equimolar amounts of the phosphane RPH_2 which was impossible to separate from the highly reactive **1**. An alternative approch was achieved by the one-pot reaction of dichlorosilane with RPH_2 in the presence of two equivalents of *n*BuLi. However, neither synthetic method gives crystalline phosphasilenes. The first synthesis of the crystalline phosphasilene **2** was achieved by a two-step reaction of $^tBuSiCl_3$ with 4 equivalents of RPHLi ($R = 2,4,6\text{-}^tBu_3C_6H_2$) and Ph_2PCl (Eq. 2) [15]. In this reaction the remarkable diphosphasila-allyl salt **2*** was first formed, representing one of the rare examples of a structurally characterized, conjugate Sila-π system.

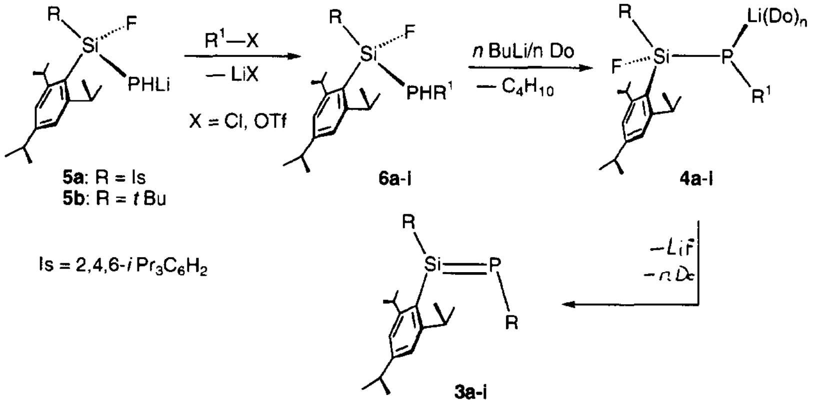


Although the molecular structure of **2** was determined by X-ray diffraction analysis (see Section 2.3), it turned out that this derivative is rather labile in solution. In order to overcome this difficulty, the phosphasilene derivatives **3** were synthesized, bearing a silyl group attached to phosphorus. Indeed, they proved to have stronger Si=P bonds (stable up to 110 °C) which has enabled study of their structures and reactivity [12].

2.1. Syntheses of P-silyl substituted derivatives 3

The synthesis of the phosphasilenes **3a–i** is achieved via the corresponding lithium(fluorosilyl)phosphanides **4a–i** by the thermally induced elimination of LiF [15]. It has been shown that perfect steric protection of the highly reactive Si=P bond in **3** is provided by the 2,4,6-triisopropylphenyl substituent (Is = isityl) attached to the low-coordinate silicon center. The appropriate precursors **4a–i** were synthesized in a multiple-step procedure, starting from **5** (Scheme 2) [12,16].

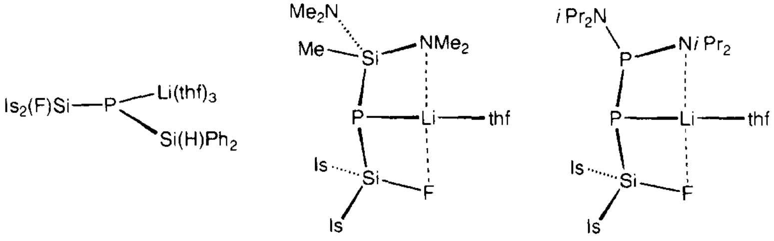
Compounds **5** were formed by the reaction of Is(R)SiF_2 (R = Is, ᵗBu) with two equivalents of [$LiPH_2$(dme)] (dme = 1,2-dimethoxyethane). They do not show the tendency to eliminate LiF in THF solutions, surely because of the strong Si–F bond. A similar stability was observed for the nitrogen analogues [10]. On silylation/germylation of **5**, compounds **6** were formed, which were subsequently lithiated on phosphorus to yield **4**. It appears that the success for the next step from **4** to **3** is dependent on different factors; however, the following three parameters may be important. (1). The reaction temperature for the elimination of LiF should not exceed 80 °C; (2) the concentration of **4** resolved in hexane or toluene is preferred in the range <0.1 mol l^{-1}; (3) the steric bulk and electronic influence of the substituent attached to phosphorus should be optimized. In the first instance, the



3, 4, 6	a	b	c	d	e	f	g	h	i
R	Is	Is	Is	Is	Is	Is	Is	Is	*t*Bu
R¹	Si*i*Pr₃	SiMe₃	Si*t*BuMe₂	SiPh₂Me	SiPh₃	Si(Naph)₃	Si*t*Bu₂H	Ge*t*Bu₂H	Si*i*Pr₃

Scheme 2. Synthesis of *P*-silylated phosphasilenes **3a–i**, proceeding via **5**, **6** and **4a–i**.

nature of the substituent at phosphorus determines the structures of the precursors **4**. This has been demonstrated by a study of a structure–reactivity relationship for several compounds **4**, including the derivatives **4j–l** [17]. The latter investigation revealed that lithiumphosphanides **4** are monomeric in solid state and solution, in which the number x of the donor solvent molecules THF attached to the lithium center ($x = 1$–3) is strongly dependent on the nature of the substituent at phosphorus. It was further observed that phenyl substituted silyl groups attached to phosphorus in **4** cause a P(n)/π^* hyperconjugation which seems to stabilize the trigonal-planar geometry around phosphorus and leads to remarkably short Si–P distances in **4j** (2.16, 2.18 Å) (Fig.1). The results of X-ray structure determinations of the related phosphanides **4j**, **4l** and **4a** are depicted in Figs. 1, 2 and 3.



4j **4k** **4l**

Scheme 3. Lithium-(fluorosilyl)phosphanides **4j–k**.

In contast to the planar coordination geometry on phosphorus in **4j**, the P atoms in **4a** and **4k** are pyramidally surrounded with the sum of phosphorus bond angles at 326.0° and 238.4°, respectively. In the case of **4f** [16] the sum of bond angles at phosphorus is 350.4° and the Si-P distances ((F)Si2–P1 2.195(4) Å, Si1–P1 2.205(4) Å) are approximately equal and identical with those observed in **4a** and **4b** [17]. Such a shortening of the Si–P distances as in **4j** ((F)Si–P 2.164(4), Ph_2HSi–P 2.186(2) Å) is not observed. Obviously, the sterically demanding tri-naphthylsilyl group at phosphorus hampered an effective hyperconjugative interaction which seems to be crucial for the trigonal-planar arrangement around phosphorus. Surprising structural features were also observed by the X-ray crystal structure of the di-tert-butylgermyl substituted lithiumphosphanide **4h** [16] (Fig. 4).

In this compound, the lithium center is chelated by one molecule DME and at the same time is attached to the phosphorus and fluorine atoms, as observed in **4k**, **l**, which causes a large pyramidalization on phosphorus (sum of bond angles 268.4°). The Li–F distance is 1.983(6) Å and is significantly shorter than in **4l** (2.060(8) Å). The Li–F bond seems to be essential in **4h** bcause of the electronic unsaturation of the Li center. This explained why the lithium center is also bound to hydrogen atoms of the tert-butyl groups at germanium in **4h**, which is supported by the relatively short Li–H distances [16].

The phosphasilenes **3a–i** were formed by heating of solutions (60–80 °C) of the corresponding derivatives **4a–i**. With the exception of **3b** ($R = SiMe_3$) and **3e** ($R = SiPh_3$) they have been isolated as yellow or orange-red oils, and in the case of **3i** as yellow crystals [12,18].

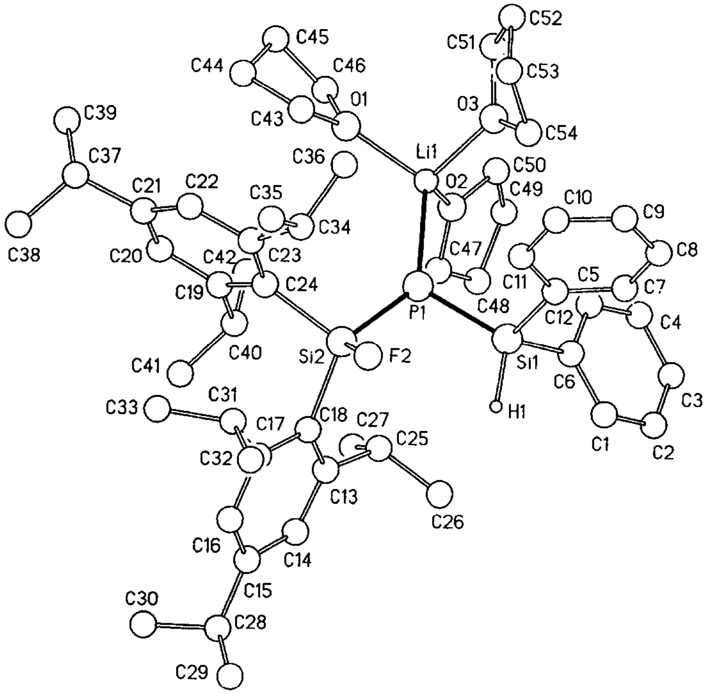


Fig. 1. X-ray crystal structure of **4j**.

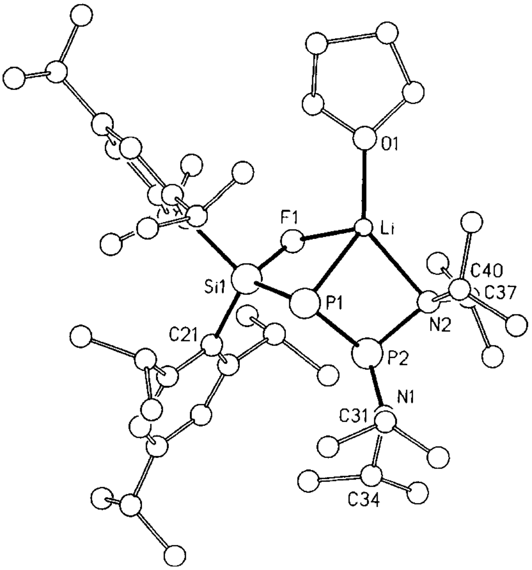


Fig. 2. Solid state structure of **4l**.

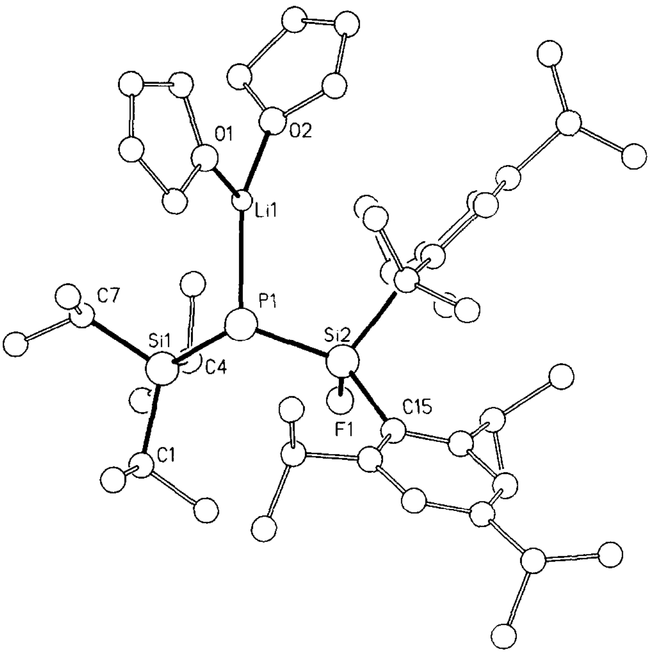


Fig. 3. X-ray crystal structure of **4a**.

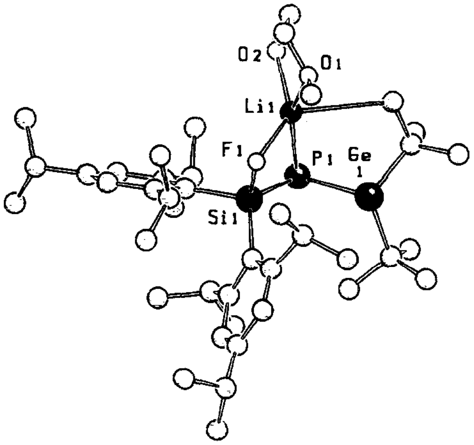


Fig. 4. X-ray crystal structure of **4h**.

2.2. *Spectroscopic characterization*

The derivatives **3a–i** exhibit characteristic ^{31}P- and ^{29}Si-NMR spectroscopic data which are summarized in Table 1. The relative large shielding for the ^{31}P nucleus, which is quite unusual for compounds bearing two-coordinate phosphorus [19], is

Table 1
^{31}P- and ^{29}Si-NMR spectroscopic data of **3a**–**3i**

^{31}P	^{29}Si	^{1}J(Si=P)	^{1}J(Si−P)	
3a	11.1[a]	167.8 (d, Si=P)	160	–
		20.8 (d, Si−P)	–	78
3b	28.1[a]	172.4 (d, Si=P)	152	–
		21.4 (d, Si−P)	–	75
3c	17.7[a]	178.4 (d, Si=P)	149	–
		14.2 (Si−P)	–	72
3d	6.8[b]	180.6 (Si=P)	154	–
		−3.7	–	70
3e	3.5[b]	181.7 (Si=P)	155	–
		−5.0 (Si−P)	–	71
3f	14.4[b]	n.o.	n.o.	–
3g	−7.8[b]	179.6 (d, Si=P)	153	–
		17.1 (d, Si−P)	–	76
3h	4.0[b]	178.9 (d, Si=P)	154	–
3i	−29.9[c]	213.2 (d, Si=P)	161	–
		21.0 (d, Si=P)	–	75

J(Si, P) coupling constants in Hz; n.o., not observed.
[a] Ref. [11]; [b] Ref. [16]; [c] Ref. 18.

noteworthy. Evidently, this is due to the strong σ-donor ability of the silyl and germyl group, and is also demonstrated by the calculated ^{31}P chemical shifts for the parent compounds $H_2Si{=}PH$ ($\delta = 85$) and $H_2Si{=}P(SiH_3)$ ($\delta = 48$) [14]. In the case of **3g**, the shielding of the phosphorus center shows the largest value in the series of phosphasilenes possessing two isityl groups at the low-coordinate silicon ($\delta = -7.8$). An even more strongly shielded ^{31}P nucleus was observed for **3i** ($\delta = -29.9$), where one isityl group is replaced by a tert-butyl group [18]. This unusual finding for **3g** and **3i** clearly indicates that both steric and electronic effects may have a considerable influence on ^{31}P chemical shifts. However, it seems clear that the ^{31}P chemical shifts are more strongly correlated by electronic than steric effects. This is shown if one compares the values of the phosphasilenes **1** and **2** with that observed for **3**. Despite the crowded aryl groups attached to phosphorus, compounds **1** and **2** possess low field ^{31}P chemical shifts in the range 65.8–136.0 ppm, as expected for their substitution pattern [20].

In the ^{29}Si-NMR spectra of **3a**–**h** (Table 1) the low-coordinate Si atoms exhibited doublets at very low field ($\delta = 167.8$ to 181.7) [12]. The unusually large shielding of the phosphorus nucleus in **3i** evidently correlates with the large deshielding of the three-coordinate silicon atom at $\delta = 213.2$, the lowest value known to date in the Si=P series [18]. The ^{1}J(Si, P) coupling constants of **3a**–**i** (149–160 Hz) are diagnostic for Si–P-π bonds, whereas much smaller values were obtained for saturated silylphosphanes [21]. In contrast, the exeptionally large ^{1}J(Si, P) value of 203 Hz for **2** indicates the special electronic nature of this derivative. This huge value may indicative of a strong interaction of the Si=P bond with the lone pair at the λ^3,σ^3-coordinate phosphorus center attached to silicon. Such an interaction is described in terms of a second-order Jahn–Teller distortion [22]. In line with this, the molecular structure of **2** (discussed below, see section 2.3) shows unusual features.

The ^{29}Si resonance signals of the SiR_3 groups lie in the expected range for saturated silicon compounds, although the ^{1}J(Si, P) coupling constants are found to be significantly larger (70–78 Hz) due to the low coordination of phosphorus. It also appears that all ^{31}P and ^{29}Si chemical shifts are significantly temperature dependent.

2.3. X-ray structure determinations

Compound **2** was the first crystalline phosphasilene derivative, whose molecular structure was elucidated by X-ray diffraction (Fig. 5) [15]. This compound exists in the (*E*)-isomeric form of a 1,3,4-triphospha-2-silabut-1-ene. The most interesting features of this structure, however, are the rather long Si=P distance (2.094(3) Å) and the significant pyramidalization of the low-coordinate silicon center (sum of silicon bond angles 356.7°). Theoretical investigations predicted shorter values (2.04–2.06 Å), and the trigonal-planar geometry around the low-coordinate silicon center for the parent compounds $H_2Si{=}PH$ and $H_2Si{=}P(SiH_3)$ [14, 23]. It was proposed that this distortion is due to steric crowding and/or an n/π^* interaction between the P2 atom and the Si=P bond. However, it is more likely that this

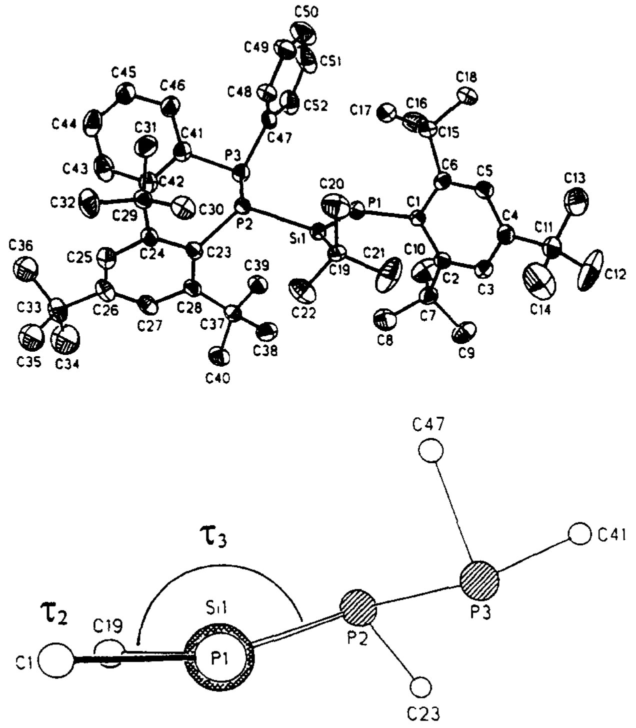


Fig. 5. Solid state structure of **2**. T_2, <C1–P1–Si1–C19, 3.4(3)°; T_3, <C1–P1–Si1–P2, 161.0(2)°.

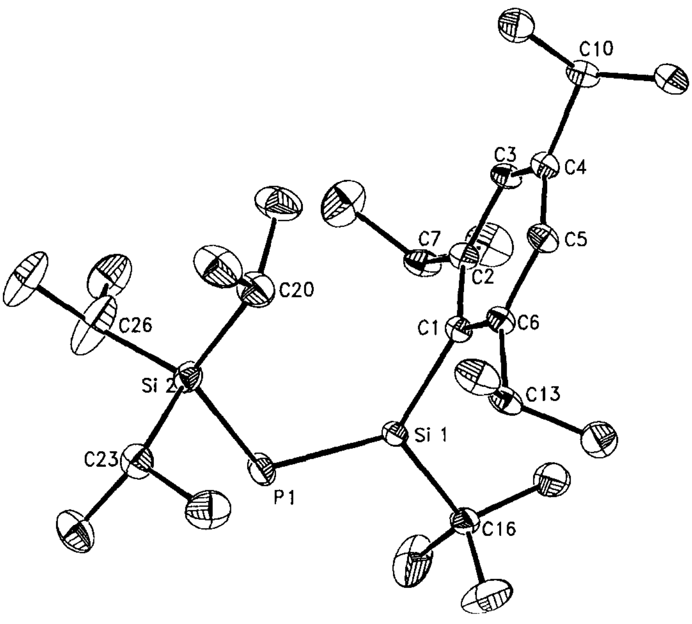


Fig. 6. X-ray crystal structure of **3i**.

structural distortion is better explained in terms of a second-order Jahn–Teller disortion, in which the HOMO (Si=P) and [LUMO + 1] (σ^* Si–P) of **2** are allowed to mix due to a small energy gap [22].

Theoretical studies have shown that phosphasilenes with silyl substituents attached to phosphorus are expected to represent Si=P bonds with trigonal-planar coordinate silicon, in which the Si–P-π bonds are strengthened by the hyperconjugative influence of the silyl group [14]. Recently, this was proved by a single crystal X-ray structure determination of **3i** (Fig. 6) [18]. Indeed, the Si=P distance in **3i** (2.062(1) Å) is significantly shorter than in **2**, and the low-coordinate silicon has a trigonal-planar geometry. The Si2–P1 single bond length (2.255(1) Å) is in the range for "normal" silylphosphanes. Both distances are in perfect agreement with respective values from ab initio calculations at a high theoretical level [14,23]. Consistent with the results of ^{31}P-CP-MAS-solid-state and solution NMR spectroscopy, the X-ray analysis proved that exclusively the (*Z*)-isomer was formed. The remarkable angle at the two-coordinate phosphorus (112.79(2)°) is considerably larger than the value predicted for $H_2Si=P(SiH_3)$ (100°) and that observed in **2** (104.2°). This seems surprising in view of the Si=P bond length in **3i** which is not significantly elongated from steric hindrance. Of considerable interest are the Si2–P1–Si1–C1 (13.7°) and Si2–P1–Si1–C16 torsion angles (169.5°) (Fig. 7), and the distinct P1–Si1–C1 (131.36(9)°) and P1–Si1–C16 bond angles (114.59(7)°). The latter surely differ for steric reasons. The geometric situation in **3i** compared to that in **2** clearly indicates that the Si=P distance and the coordination geometry at silicon is more strongly influenced by electronic than steric effects.

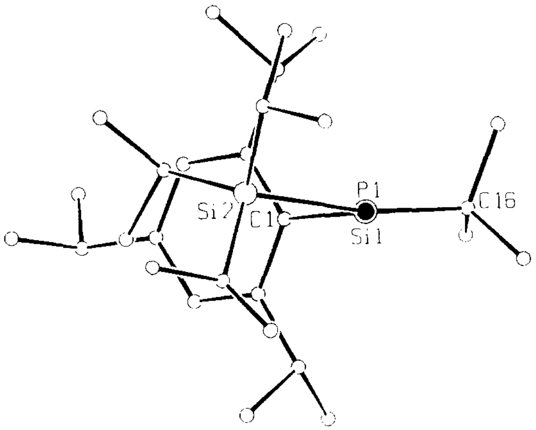


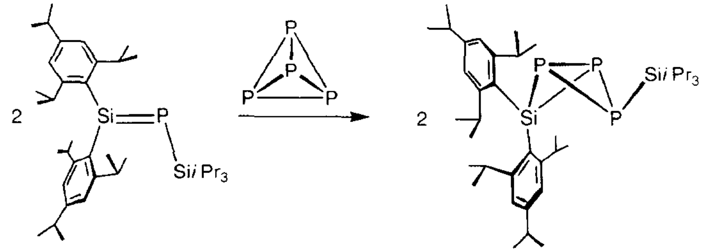
Fig. 7. View of **3i** along the Si=P vector.

2.4. *Some chemical properties of 3*

The remarkably high thermal stability of the phosphasilenes **3** (exceptions **3b** and **3e**) (up to 110 °C) enabled us to investigate the reactivity of the Si=P bond. Thus the oxidation reaction of **3** with white phosphorus and elemental chalcogenes (S, Te) was studied, and a series of cycloaddition reactions with unsaturated organic molecules were performed [16]. The reactivity of the representative derivative 3a is discussed below.

2.4.1. *Oxidation with white phosphorus, elemental sulfur and tellurium*

It was recently reported that tetramesityldisilene ($Mes_2Si=SiMes_2$) reacts with P_4 to give the 2,2,4,4-tetramesityl-1,3-diphospha-2,4-disilabicyclo[1.1.0]butane [24]. This process is remarkable because Si–P bonds, which are usually generated by salt elimination reactions starting from alkalimetal phosphanides and halogenosilanes, were formed under fairly mild conditions (40 °C). It is further noteworthy that during the reaction of the Si=Si bond with P_4 both the π- and σ-bonds between the Si atoms were cleaved. Consistently, we have shown that, besides disilenes, phospha- and arsa-silenes are the only known compounds with (p–p) π bonds between main group elements which degrade P_4 under such mild conditions [12]. Thus **3a** reacts with P_4 in the molar ratio of 2:1 to give the SiP_3-butterfly-like compound **7** (Eq. 3).



(3)

3a **7**

The ^{31}P- and ^{29}Si-NMR spectra of 7 (Fig. 8(a,b)) indicate that it prefers the exo configuration at 25 °C [12].

At higher temperature (above 38 °C) the inversion of configuration of the peripheral phosphorus atom was observed in the ^{31}P-NMR spectrum, that is, 7 rearranges into the endo isomer 7* and vice versa (Scheme 4) [12,16].

An inversional barrier of 23 kcal mol^{-1} has been estimated for this process. From MO calculations of P_2Si_2-bicyclo[1.1.0]butanes [25] we assume that the SiP_3 system also has a very high barrier to ring inversion (Scheme 4). Therefore the temperature dependence of the ^{1}H-, ^{31}P- and ^{29}Si-NMR spectra of 7 seems to be caused by dynamic effects of the isityl groups at silicon (hindered rotation of aryl rings), as well as inversion of the peripheral P atom.

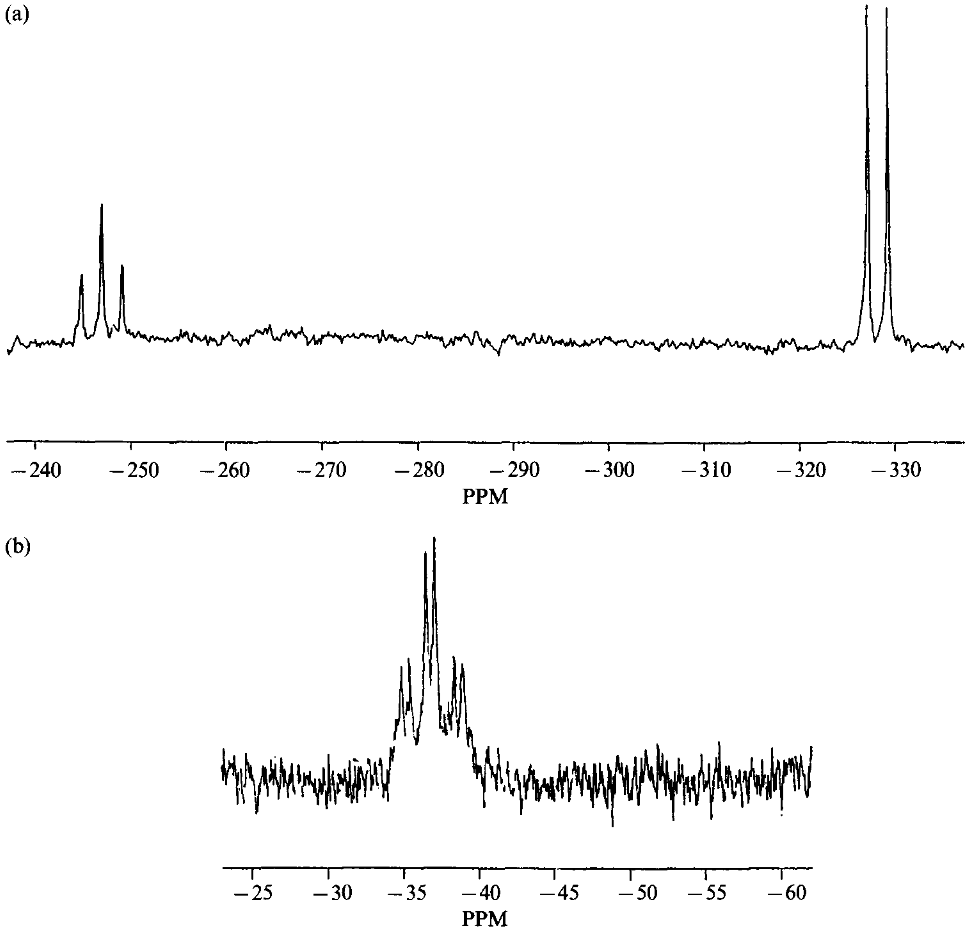
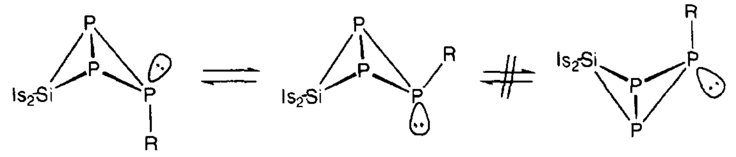
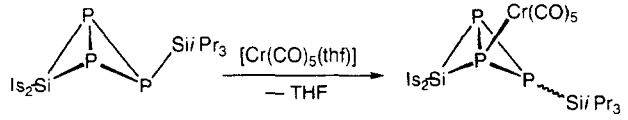


Fig. 8. (a) ^{31}P-NMR spectrum of the SiP_3-butterfly-like molecule **7a**. (b) Resonance signal of the silicon ring atom of **7a** (^{29}Si-NMR).



Scheme 4. Isomerization of **7** by phosphorus inversion.

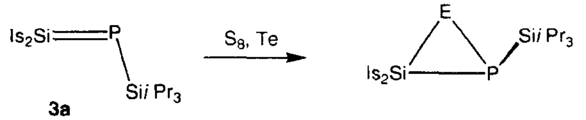
The reaction of **7** with [Cr(CO)$_5$(thf)] leads to the mono-pentacarbonyl-chromium complex **8**, even if the components are mixed in the molar ratio 1:3 (Eq. 4) [16].



(4)

Obviously, the bulky SiPr$_3$ group attached to the peripheral phosphorus center prevents the formation of a bis-chromium complex. In contrast, the Si$_2$P$_2$-butterfly-like compound 2,2,4,4-tetramesityl-1,3-diphospha-2,4-disilabicyclo-[1.1.0]butane gives the respective *P,P'*-bis(pentacarbonylchromium) complex in which the chromium centers are attached to the two bridgehead P atoms [24]. In **8**, the chromium atom is also bound to a bridgehead phosphorus atom. This has been proved by the ^{31}P-NMR spectrum, in which three sets of signals are representing an ABM-spin system (A=B=M=^{31}P).

The oxidation of **3a** with elemental sulfur and tellurium led quantitatively to the three-membered heterocycles **9** and **10**, respectively (Eq. 5) [16].



(5)

The latter do not yield 1,3-dichalcogen-2,4-phosphasila-cyclobutanes if reacted with an excess of elemental sulfur and tellurium. The composition of **9** and **10** was proved by mass spectrometry and their constitution was deduced from ^{31}P-, ^{29}Si- and ^{125}Te-NMR spectroscopic data [16].

2.4.2. Reactivity toward alkynes and cyclopentadiene

The behavior of the Si–P-π bond in **3a** toward a C≡C triple bond was examined, employing different substituted alkynes [16]. It appeared that **3a** does not react with dialkyl-, diaryl- or disilyl-substituted alkynes at 110 °C; even cyclooctyne (a very reactive alkyne) does not react. However, if **3a** is stirred with phenylacetylene at 80 °C in toluene the C–H insertion product **11** is formed and isolated as colorless crystals (Eq. 6). Its molecular structure has been elucidated by single crystal X-ray diffraction (Fig. 9).

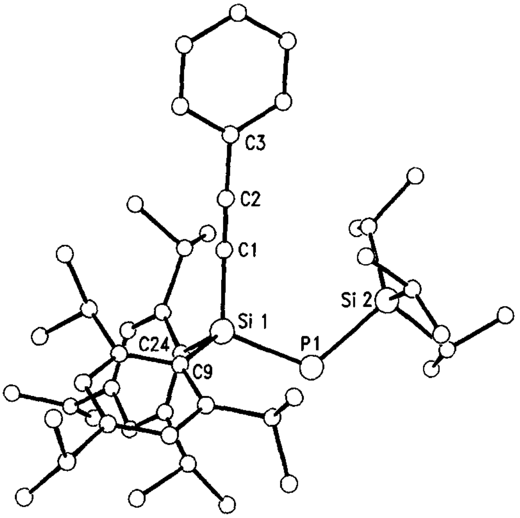


Fig. 9. Solid state structure of **11**.

It appears that, according to the bond polarity in the Si=P bond (Si^+–P^-), the acetylene moiety has been added to the Si atom and the phosphorus atom protonated. The sterically demanding $SiPr_3$ group at phosphorus causes an unusually large Si1–P1–Si2 bond angle (116.0(2)°). It is interesting to note that the reaction of tetramesityldisilene (Si=Si) with phenylacetylene yields the [2+2]-cycloadditional product 1,1,2,2-tetramesityl-3-phenyl-disilacyclobut-3-ene exclusively [26]. Experiments to convert **11** into the corresponding silaphospha-heterocyclobut-3-ene **12** (Eq. 6), by means of AIBN (azodiisobutyronitrile) as a radical starter for hydrophosphinations, were unsuccessful.

The ability of the Si=P bond to serve as a dienophile for a [2+4]-cycloaddition (hetero-Diels–Alder reaction) has been verified by the reaction of **3a** with cyclopentadiene (Eq. 7) [16]. The components react at 60 °C in benzene to give **13** quantitatively, which was isolated as colorless solid. Interestingly, a Brønsted acid-(C–H)-base- (Si=P) reaction, as in the case of **3a** and phenylacetylene, was not observed. In the mass spectrum of **13** the molecular peak and the "free" phosphasilene $\mathbf{3a}^+$ have been detected. Similar behavior was observed for related adducts (such as from Ge=P bonds onto hetero-butadienes [27]).

2.4.3. *Reactions with benzophenone and 1,2-diphenyl-1,2-diketone*

The Si=P bond in **3a** readily reacts with benzophenone at −80 °C to form the heterocyclobutane **14** (Eq. 8) [16]. In contrast, no reaction occurs in the case of $^tBu_2C{=}O$. The molecular structure of **14** was determined by X-ray analysis (Fig. 10), which revealed that the compound is isotypic to the arsenic homologue [13,16]. The four-membered SiOPC framework is a puckered (along the SiC axis 16.9°) distorted trapezoid due to the different bond lengths in the skeleton. A remarkably long P–C distance (1.945(6) Å) is observed, which is surely caused by steric hindrance.

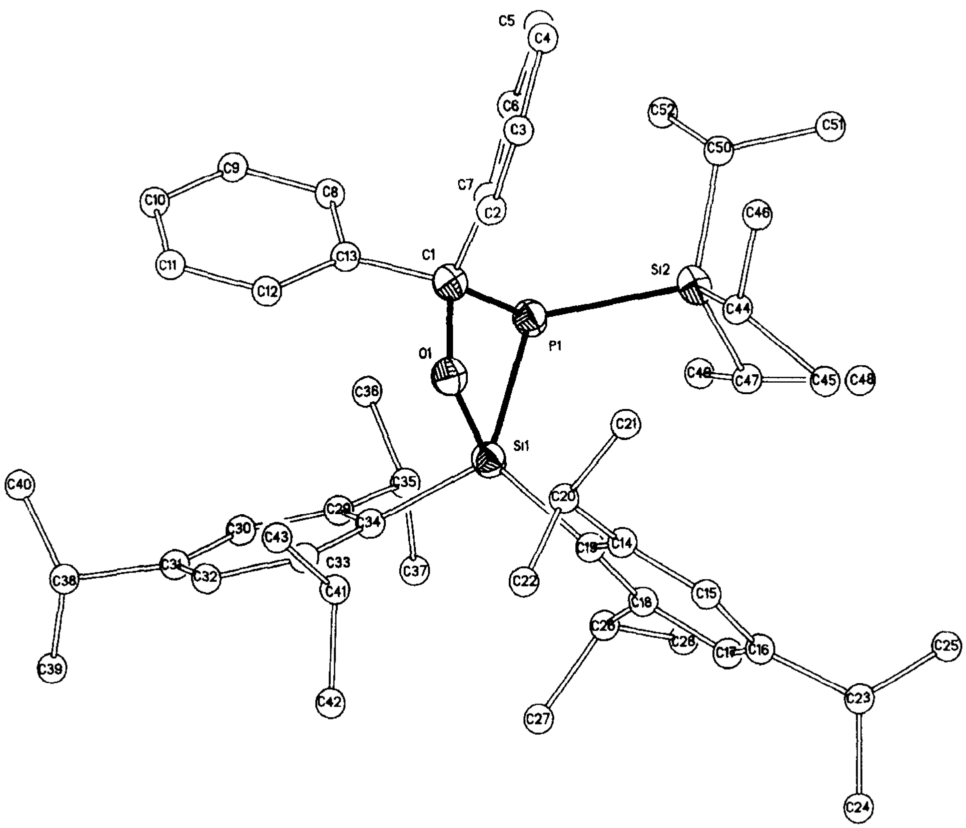


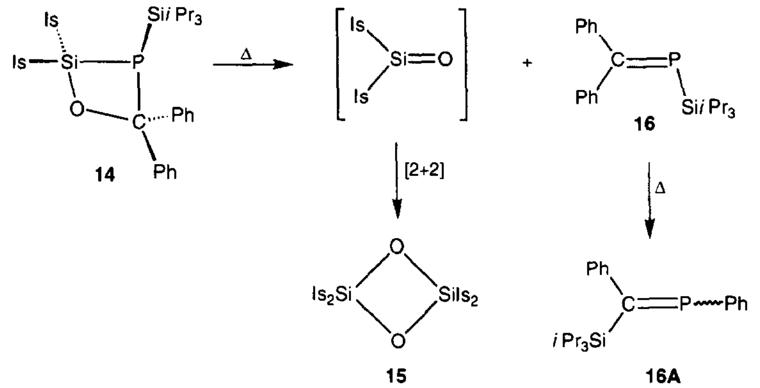
Fig. 10. X-ray crystal structure of **14**.

Endocyclic P–C bonds in 1,3-diphosphacyclobutanes are usually in the range 1.87–1.91 Å [28]. The sum of bond angles at phosphorus in **14** is 290.8°, that is the P atom is pyramidal.

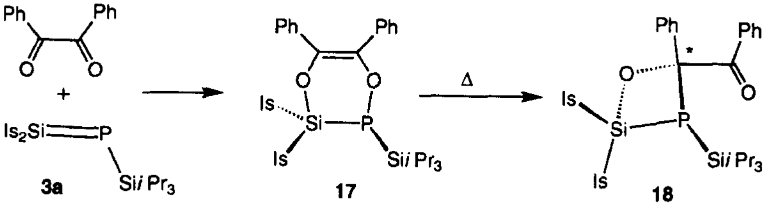
It appears that **14** actually decomposes if heated at 160 °C, in a sila-Wittig-type reaction, into the transient silanone $Is_2Si{=}O$, which immediately dimerizes to **15**, and the phosphaalkenes **16** and **16A** (Scheme 5) [16].

Compounds of type **15** are well known from the work of West et al. [29]. Because of the drastic reaction conditions, it is understandable that **16** ($\delta = 293.7$) partially isomerizes to **16A** ($\delta = 281.9$) although such an isomerization process was previously unknown for phosphaalkenes. Furthermore, the Si=P bond possesses a remarkable reactivity toward 1,2-diphenyl-ket-1,2-dione. If **3a** is allowed to react with PhC(O)–C(O)Ph at 25 °C, surprisingly, the [2+4]-cycloadduct **17** ($\delta(^{31}P) = 116.3$) was formed only in 10% yield (Scheme 6) [16]. Diastereomerically pure colorless plates of the [2+2]-cycloadduct **18** ($\delta(^{31}P) = -32.9$) was isolated as the major product of the latter reaction.

On heating of the reaction mixture at 110 °C compound **17** was completely rearranged



Scheme 5. Transformation of **14** into **15** and the diastereomeric phosphaalkenes **16** and **16A**, respectively.



Scheme 6. Synthesis of **17** and **18**.

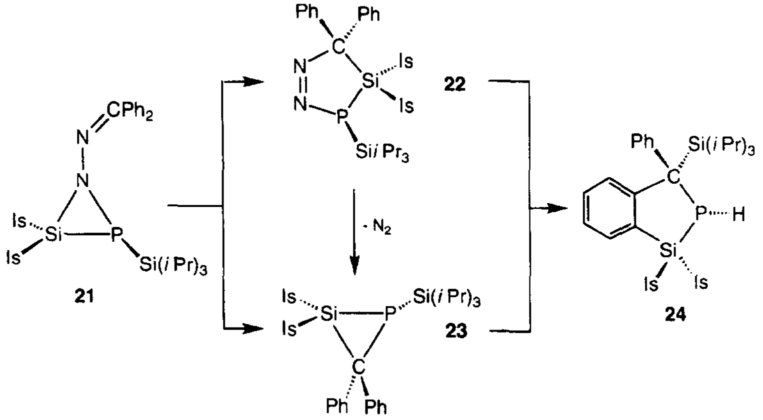
to **18** (^{31}P-NMR), indicating that **18** is the thermodynamic product. We assume that this is due to ring strain (C=C bond in the six-membered C_2O_2SiP-ring).

2.4.4. Reactions with mesitylazide, diphenyldiazomethane, isocyanides, and phenylcyanide

Compound **2a** reacts with mesitylazide readily at −80 °C in toluene, to give a deep red-purple solution. The ^{31}P-NMR spectrum revealed formation of the compounds **19** and **20** (Eq. 9) [16,30]. Compound **19** was completely transformed into **20** after heating of the reaction mixture at 40 °C. The ^{29}Si-NMR data for **19** (doublet at −16.7, $^1J(\mathrm{Si, P}) = 43.8$ Hz) clearly prove that this primary product was not a [2+1]-cycloadduct of **3a** with azide, as disilaaziridines show characteristic ^{29}Si-NMR chemical shifts at −50 to −54.2 [31]. Replacement of one silicon atom by phosphorus in the three-membered ring skeleton as in **20** results in a very similar shielding of the ^{29}Si nucleus to −64.7 ($^1J(\mathrm{Si, P}) = 38.4$ Hz). The ring isomerization of **19** into **20** clearly also has a significant influence onto the ^{29}Si chemical shifts and ^1J(Si, P)-coupling constants of the Si atom of the $SiPr_3$ group (**19**: $\delta = 17.1$, $^1J = 87.3$ Hz; **20**: $\delta = 11.9$, $^1J = 114.2$ Hz).

In contrast to the reaction of the Si=P bond with mesitylazide, the reaction of **3a** with diphenyldiazomethane surprisingly gives the [2+1]-cycloadduct **21** (Scheme 7) [32].

The bonding situation in **21** (Fig. 11) may be described in terms of a π-complex,



Scheme 7. Formation of **21** and its rearrangement reactions into **22**, **23** and **24**.

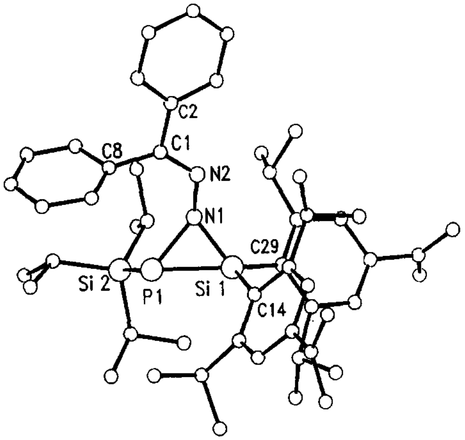


Fig. 11. X-ray crystal structure of **21**.

employing the Dewar–Chatt–Duncanson model, in which the Si=P bond acts as π donor and acceptor at the same time (Scheme 8). The corresponding [2+3]-cycloaddition product **22** was only generated on thermic activation of **21**. Further heating of **22** at 110 °C yielded the hetero-cyclopropane **23** by elimination of N_2 and finally the unusual constitutional isomer **24** was formed [30,32]. Its structure was established by X-ray diffraction analysis (Fig. 12).

The unusual reactivity of the Si=P bond in **3a** was further demonstrated by its behavior toward mesitylisocyanide [16,33,34]. In this process, two equivalents of isocyanide were consumed even if **3a** was used in a equivalent molar ratio, and the unusual heterocycle **25** with an exocyclic imino and phosphaalkenylidene group was formed (Eq. 10); a reaction intermediate was not detected by NMR spectroscopy. Analogous results were obtained by the reaction of **3a** with 1,6-diisocyanohexane, from which the macroheterocycle **26** was isolated (Fig. 13) [34]. The P=C distance

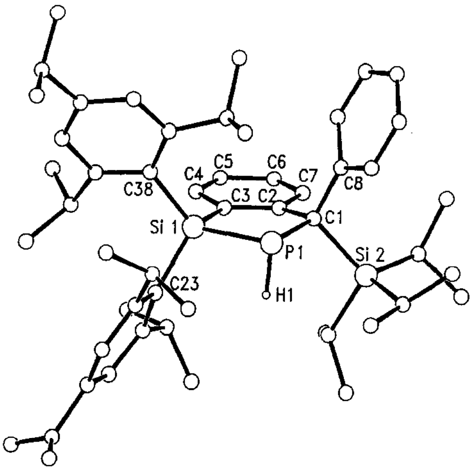
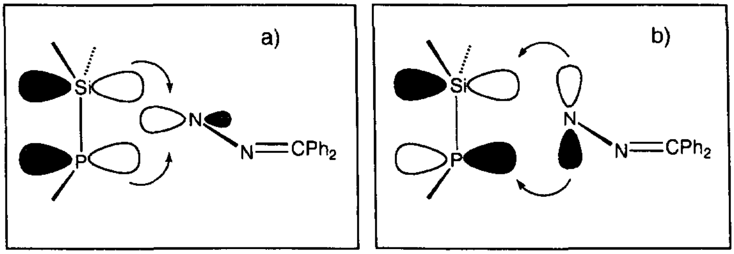


Fig. 12. Solid state structure of **24**.



Scheme 8. Description of **24** as π-complex (Dewar–Chatt–Duncanson model). (a) Si=P bond as π-donor, (b) Si=P bond as π-acceptor.

(1.698(4) Å) in **26** reflects the slight stabilization of the π bond by conjugation with the exocyclic C=N bond.

The latter results indicate that phosphasilenes react in a similar fashion to silenes (Si=C) (similar polarities of the Si=E bonds!) [35]. Interestingly, during the analogous reactions of silenes with isocyanides the isolation of intermediates was achieved. The Si=Si bond in disilenes, however, reacts with two equivalents of isocyanide in a stepwise process to yield firstly silacyclopropanimines [36] and secondly 1,3-disilacyclobutan-2,4-diimines [37].

Futhermore, the Si=P bond in **3a** reacts with organocyanides in a [2+2]-cycloaddition fashion. Thus the reaction of **3a** with phenylcyanide readily takes place at 25 °C, and the phosphaazasilacyclobut-3-ene 27 is formed in quantitative yield [16]. Analogous adducts, generated by the reaction of cyanides and disilenes, are also known [38]. It was somewhat surprising that the even more reactive C≡P triple bond in tert-butyl-phosphaacetylene does not react with phosphasilenes but with the Si=As bond in arsasilenes (see section 3.3.3.).

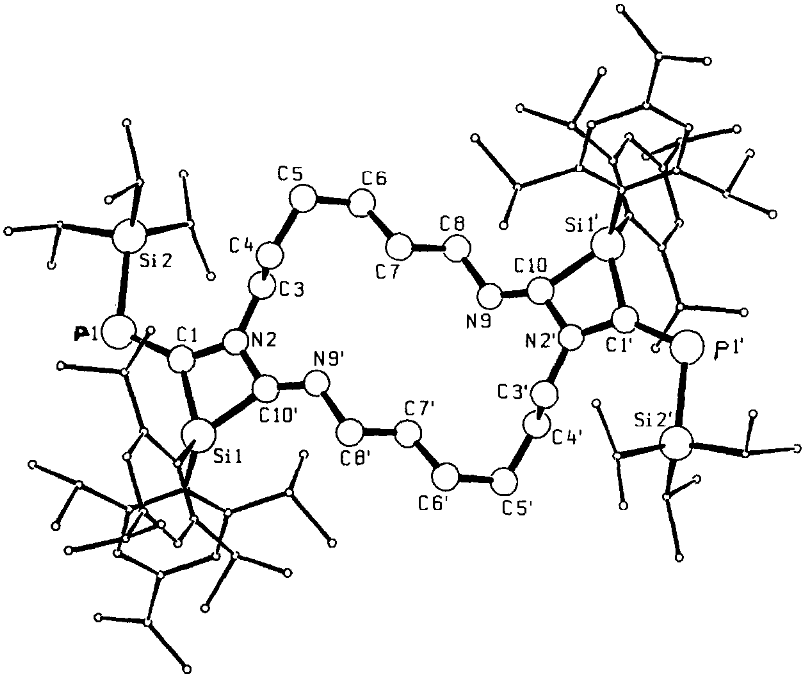


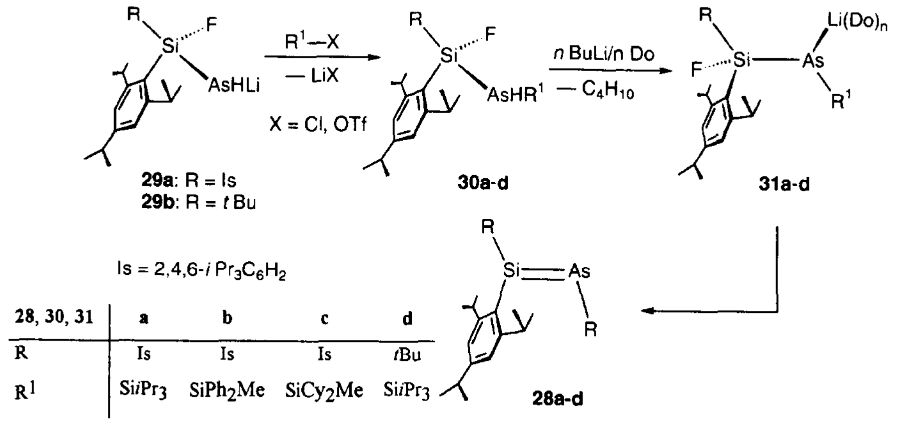
Fig. 13. Molecular structure of **26**.

3. Stable silylidene-arsanes

3.1. Synthesis and spectroscopic properties

The synthesis of compounds containing a Si=As bond was achieved by a route analogous to that used for the phosphasilenes **3** (Scheme 9) [13,16]. Thus the thermolysis of colorless solutions of **31a–d** in hexane at 60 °C yielded the desired products **28a–d** as orange-red oils or orange solids. The starting materials for the formation of **31a–d** (**29a**, **b** and **30a–d**) were generated in an analogous fashion to **6a**, **b** and **4a–i** (Scheme 2), and used directly without isolation.

The arsasilenes **28a–d** can be heated up to 100 °C for several days without decomposition. Their structures were unambiguously determined by ^{29}Si NMR spectroscopy [13,16]. As for the analogous phosphasilenes, the low-coordinate Si atom gives singlet signals at very low field: $\delta(^{29}\mathrm{Si}, 296\ \mathrm{K}) = 179.1$ (**28a**), 183.6 (**28b**), 187.0 (**28c**), and the most deshielding signal has been detected for **28d** ($\delta = 228.8$) [18]. As observed for phosphasilenes, the ^{29}Si chemical shifts of **28a–d** are strongly temperature dependent. Remarkably, the Lewis-donor ability of the solvent used does not significantly influence the ^{29}Si chemical shifts; the same is true for Si=P compounds. This is in contrast to the behavior of silanimines (Si=N), which form donor solvent adducts [9]. An (*E*)/(*Z*)-isomerization has not yet been observed for either type,



29a: R = Is
29b: R = *t*Bu

30a-d

31a-d

28a-d

Is = 2,4,6-*i* $\mathrm{Pr_3C_6H_2}$

28, 30, 31	a	b	c	d
R	Is	Is	Is	*t*Bu
R^1	$\mathrm{Si}i\mathrm{Pr}_3$	$\mathrm{SiPh_2Me}$	$\mathrm{SiCy_2Me}$	$\mathrm{Si}i\mathrm{Pr}_3$

Scheme 9. Synthesis of the arsasilenes **28a–d**.

phospha- and arsa-silenes. We assume that this process is hampered by steric hindrance in these derivatives.

3.2. *Molecular structure*

The X-ray structure determination of the first crystalline arsasilene **28d** (Fig. 14) revealed a Si=As distance of 2.164 Å, and a Si–As single bond distance of 2.363 Å [18]. These values are in perfect agreement with the respective calculated bond lengths in $H_2Si{=}As(SiH_3)$ [14]. The low-coordinate silicon center has a trigonal-

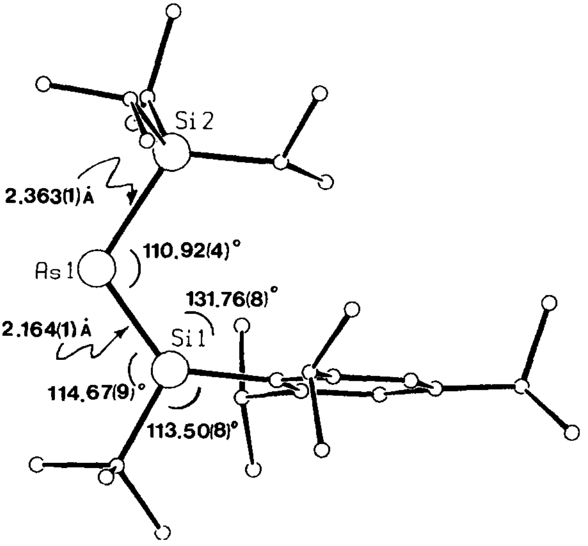


Fig. 14. X-ray crystal structure of **28d**.

planar geometry as in the case of the phosphorus analogue **3i**. The bond angle at arsenic (110.92(4)°) is slighlty smaller than the corresponding value at phosphorus in **3i** (112.79(4)°). This is explained by the larger arsenic atom compared to phosphorus. However, the bond angles at the silicon center in **28d** remain unchanged in comparison with the values observed in **3i**.

3.3. Some chemical properties

Recently we reported on the chemical behavior of the Si=As bond in **28a** toward tellurium, benzophenone and organoisocyanides [13,33,34]. The results indicate that the reactivity of the Si=As bond is very similar to that of the Si=P bond. However, we found that the Si=As bond shows a quite different thermolysis behavior, and is more reactive than the Si=P bond. The latter was demonstrated by the [2+2]-cycloaddition of the Si=As bond onto the C≡P triple bond in phosphaalkynes (see Section 3.3.3). In this section we describe the thermolysis behavior of **28a**, the reaction of **28a** with P_4, and the characterization of new cycloaddition products from reactions of **28a** and **28c** with Ph_2CN_2, PhCN and ^{t}BuCP.

3.3.1. Thermolysis of the Si=As bond

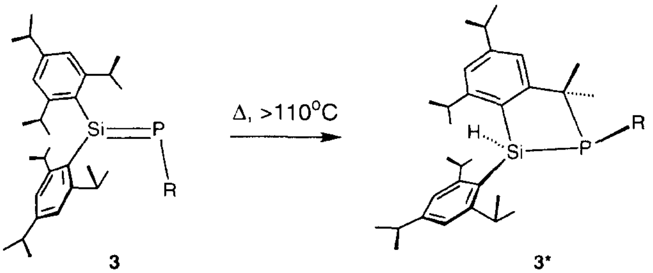
It was observed that both the Si–As-σ and -π bond are broken on heating, but the products from this process could not yet be identified. Interestingly, insertion of the Si–As-π bond into a C–H bond of one *ortho*-isopropyl group, as obtained in the case of phosphasilenes (Scheme 10) [39], was not observed. An Si–H bond was not evident in the ^{29}Si NMR spectrum of the crude product.

However, thermolysis in the presence of triethylsilane produced **32** and **33**, which clearly demonstrates the formation of silandiyl and arsandiyl as transient intermediates during this process (Scheme 11), and indicates that the Si=As bond is intrinsically less stable than the Si=P bond.

This reflects the instability of "double bonds" (X=Y) between heavier main group elements with respect to the corresponding single bonds (X–Y).

3.3.2. Oxidation with white phosphorus

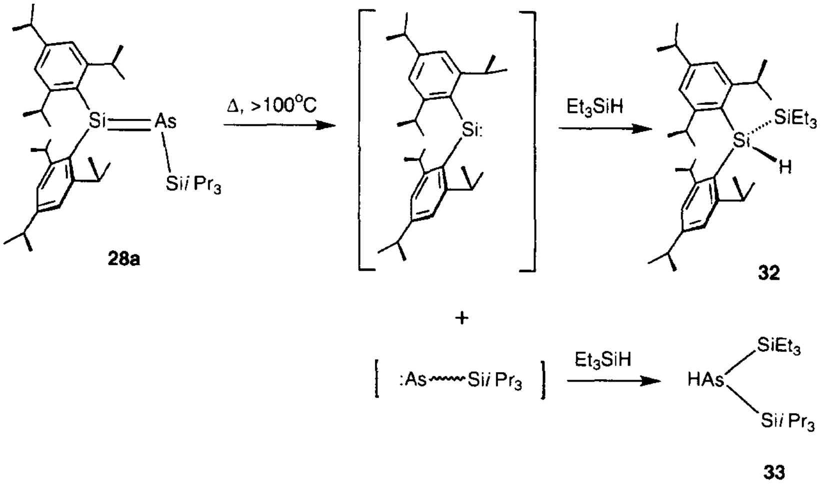
The transformation of **28a** with P_4 in the molar ratio 2:1 occurs readily at 40 °C, and a complicated product mixture is formed. On heating this mixture for 2 days at



3

3*

Scheme 10. Thermolysis of the Si=P bond in 3.



Scheme 11. Formation of **36a,c**, **37a,c** and **38a,c** by reactions of **28a,c** withPh$_2$CN$_2$, PhCN and ^{t}BuCP.

100 °C, the butterfly-like compounds **34** ($\delta = -312.5$) and **35** ($\delta = -231.7$, -299.7, ^1J(P, P) = 183 Hz) were generated (Eq. 12) [16]. The molar ratio of these compounds was approximately 3:2. They could not be transformed into each other, and the separation of the isomers has not yet been successful. Evidently, the initial product mixture, containing phosphorus-rich polycyclic compounds, degrades into the bicycles **34** and **35**. Similar product mixtures, the structures of which have been established, were also observed by the analogous transformation of (*E*)-1,2-di-tert-butyl-1,2-dimesityldisilene and tetramesityldisilene with white phosphorus and yellow arsenic (As$_4$), respectively [24,40].

3.3.3. Reactions with diphenyldiazomethane, phenylcyanide and tert-butyl-phosphaacetylene

During the addition of Ph$_2$CN$_2$ to a solutions of **28a,c** in toluene at −78 °C, the intense purple color of the diazomethane disappeared and the yellow, crystalline [2+1]-cycloadducts **36a,c** were isolated (Scheme 12) [16]. The molecular structure of **36a** was elucidated by X-ray diffraction analysis (Fig. 15).

Compound **36a** is isotypic to the analogous phosphorus derivative **21**. In comparison to the Si–As distance in the [2+2]-cycloadduct derived from **28a** and benzophenone (2.38 Å) [13], the Si1–As1 bond length in **36a** is slightly shorter (2.353(5) Å). The endocyclic angle at arsenic is 45.3°, and is therefore significantly smaller than the corresponding value at phosphorus observed in **21** (49.2°).

From reactions of **28a,c** with phenylcyanide and tert-butyl-phosphaacetylene we were able to demonstrate that the Si=As bond easily forms [2+2]-cycloaddition products with main group element triple bonds [16]. However, as in the case with Si=P bonds, the Si=As bond does not react with the C≡C triple bond in alkynes.

The structures of compounds **37a,c** and **38a,c** were established by means of NMR spectroscopy and mass spectrometry. Due to the different polarity of the C≡N and

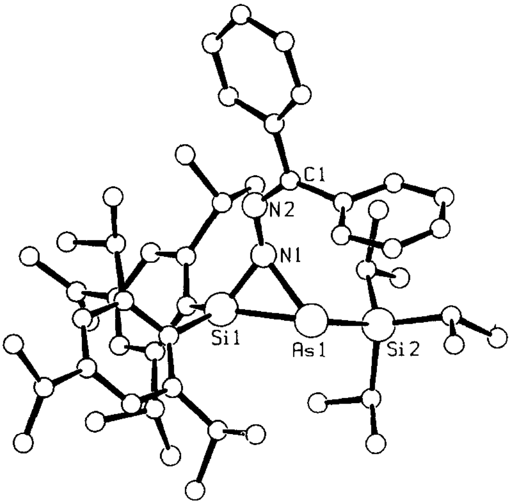


Fig. 15. Solid state structure of **36**.

C≡P triple bonds, the silicon ring atom in **37a,c** is bound to the nitrogen atom, and in **38a,c** to the carbon atom of the C≡P moiety. The molecular structure of **37c** was further determined by a single crystal X-ray diffraction analysis (Fig. 16) [16]. The four-membered SiNAsC framework is slightly puckered (folding angle N-Si-C/Si-C-As 7°), and the As–Si distances (2.402(2) and 2.397(2) Å) are in the

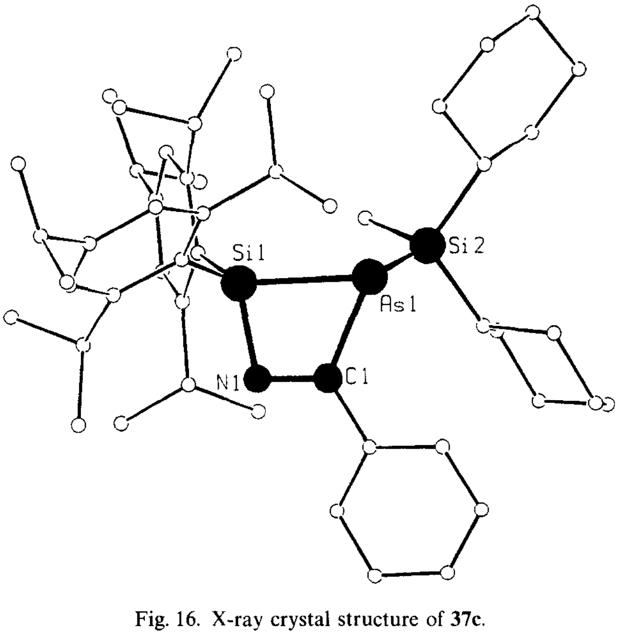


Fig. 16. X-ray crystal structure of **37c**.

expected range for single bonds. However, the As–C bond length (1.988(6) Å) and the endocyclic arsenic bond angle (65.1(2)°) are significantly smaller than the respective values in **14**. Evidently, the short C1–N1 distance (1.292(7) Å) in **37c** forced a rather small endocyclic bond angle at silicon (80.9(2)°). The different bond lengths in the ring causes distinctly smaller angles at the carbon and nitrogen ring atoms in comparison to the ideal value of 120° (112.2(4) and 101.3(4)°, respectively).

Acknowledgements

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