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# Synthesis and molecular structure of fluoro(triphosphanil)silane and attempts to synthesize a silylidyne–phosphane

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Dedicated to the memory of Professor Marianne Baudler

## Abstract

The synthesis, isolation, spectroscopic characterization (IR, multi-nuclear NMR) and single-crystal X-ray diffraction analysis of  $\text{FSi}(\text{PH}_2)_3$  (**1a**), the first isolable fluorophosphanisilane, is reported along with the gas phase decomposition of **1a**,  $\text{MeSi}(\text{PH}_2)_3$  (**1b**) and  $\text{EtSi}(\text{PH}_2)_3$  (**1c**) under flash vacuum or pulsed pyrolysis conditions and matrix isolation of the products. The title compound is formed quantitatively by  $\text{PH}_2/\text{F}$ -ligand exchange reaction of tetraphosphanisilane  $\text{Si}(\text{PH}_2)_4$  with the difluorodiarlylstannane  $\text{I}_2\text{SnF}_2$  ( $\text{I} = 2,4,6\text{-triisopropylphenyl}$ ) in the molar ratio of 1:1 in benzene as solvent. Since **1a** cannot be separated from the solvent by fractional condensation its isolation was achieved by means of preparative GC. A single crystal of **1a** (triclinic,  $P\bar{1}$ ) suitable for X-ray diffraction analysis was grown by in situ crystallization on a diffractometer at 175 K through miniaturized zone melting with focused infra-red radiation. Interestingly, the Si atom is remarkably distorted tetrahedral coordinated with F–Si–P angles of 120.4(7), 110.4(7), 106.3(1)° and normal Si–F (1.60(2) Å) and Si–P distances (av. 2.241(2) Å). According to ab initio (MP2/6-31G(d,p); MP2/6-311G(2d,p)) and DFT calculations (BLYP, B3LYP, B3PW91 functionals), the distortion is not an intrinsic property of the molecule but due to crystal packing forces. The best agreement between the experimental versus calculated geometrical and vibrational data is achieved at the B3PW91/6-311G(2d,p) level of theory. Since **1a–c** appeared as potential precursors for the respective silylidyne–phosphanes ('silaphospha–acetylene')  $\text{RSiP}$  through stepwise extrusion of  $\text{PH}_3$ , some thermodynamical data for the decomposition and the relative energies of linear  $\text{RSiP}$  versus bent  $:\text{SiPR}$  isomers ( $\text{R} = \text{H}, \text{Me}, \text{Et}, \text{Pr}, \text{Ph}, \text{CF}_3, \text{OMe}, \text{halogen and SiH}_3$ ) were also calculated. The latter revealed that electronegative substituents R favor the Si–P triple bond in  $\text{RSiP}$  (except for  $\text{R} = \text{CF}_3$  which stabilizes the  $:\text{SiPR}$  form) while strong  $\sigma$ -donating substituents R ( $\text{H}, \text{SiH}_3$ ) favor the  $:\text{SiPR}$  isomer with Si=P double bond. Although elimination of  $\text{PH}_3$  and other fragmentation products could be detected by controlled thermal decomposition and matrix isolation, neither flash vacuum experiments of **1a**, **1b** and **1c** (400–600 °C) nor pulsed pyrolyses of **1a** at (1100 °C) did provide any direct evidence for the formation of the desired species with Si–P multiple bonds.

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**Keywords:** DFT calculations; Flash-vacuum-pyrolyses; Fluorosilanes; Silicon–phosphorus compounds; Silylidyne–phosphanes

## 1. Introduction

During the last 20 years, the chemistry of low-coordinated heavier main-group elements (e.g. Si, Ge, Sn, P, As, Sb, Bi) has experienced a tremendous

progress. Nowadays even inert compounds containing Si=E double bonds (E = main-group elements) [1] are no longer laboratory curiosities but common versatile starting materials for the synthesis of a large variety of novel classes of silicon-heteroatom compounds. For example, we have shown that the synthesis of chemically inert Si=P and Si=As compounds (silylidene–phosphanes and –arsanes, 'phospha- and arsa-silenes') succeeds with sterically congested organic groups at

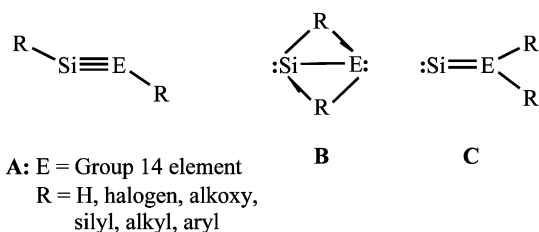
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E-mail address: [matthias.driess@ruhr-uni-bochum.de](mailto:matthias.driess@ruhr-uni-bochum.de) (M. Driess).

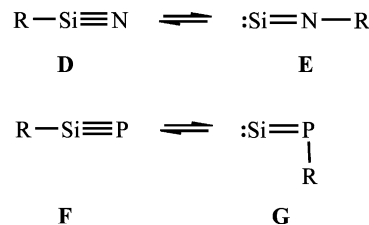
silicon and their stabilization is drastically increased with triorganosilyl groups at phosphorus and arsenic [1c,2]. One of the present challenges and efforts in main-group chemistry is the synthesis of compounds containing silicon-element triple bonds, so-called silylidyne [3]. However, the synthesis of compounds with the composition  $R_2SiE$  ( $E =$  group 14 element) is particularly delicate because they can exist in the form of several isomers with non-classical geometries (Scheme 1) [4]. Thus, the alkyne-analogues **A** with Si–C and Si–Si triple bonds are calculated to prefer a non-linear  $RSiER$  arrangement due to the reluctance of silicon to undergo  $sp$ -hybridization.

Interestingly, the bridged structure **B** for  $H_2Si_2$  has been confirmed by microwave spectroscopy [5]. Fortunately, substituent effects seem to direct the stabilities of **A**, **B** and **C**. Thus, strong electronegative (halogen, alkoxy) ligands or steric congestion at silicon favor the form **A** on the energy potential surface. Recently, Schwarz et al. have proven indirectly the formation of the alkylidyne–silane  $XSiCH$  ( $X = F, Cl$ ) in the gas phase [6], while spectacular results by Wiberg et al. revealed evidence for the existence of the first inert disilyne with a Si–Si triple bond (form **A**) [7]. It is further expected that isovalence electronic compounds of the type  $RSiE$  (Silylidyne–amines, –phosphanes, and –arsanes) can also exist in different valence isomeric forms (Scheme 2).

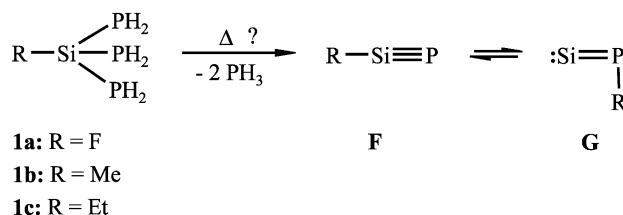
Because of the different electronegativity of nitrogen and phosphorus, the situation for the equilibrium in the cases of silylidyne–amines **D** (azyne–silane, ‘silacyanide’)/**E** (imino–silylidene, ‘silaisocyanide’) [8] and silylidyne–phosphanes **F** (silylidyne–phosphane)/**G** (silylidene–phosphylidene) [9] is strongly substituent-dependent. While the parent silylidyne–amine **D** and the silaisocyanide:SiNPh (form **E**) could be detected by matrix isolation spectroscopy [10] and photoelectron spectroscopy [11], silylidyne–phosphanes are hitherto unknown. We are currently investigating suitable methods for the synthesis of silylidyne–phosphanes. Since phosphanylsilanes are thermally labile and evolve  $PH_3$ , it seemed tempting to use triphosphanylsilanes (**1**) as potential precursors for the thermal synthesis of silylidyne–phosphanes via flash vacuum pyrolysis (FVP) or related techniques, according to Scheme 3.



Scheme 1. Different valence-isomers of  $R_2SiE$ .



Scheme 2. Valence-isomers of  $RSiN$  and  $RSiP$  compounds.



Scheme 3. Proposed decomposition of **1a**, **1b**, **1c** to **F** and **G**.

We present here the synthesis and structure of the fluoro(triphosphanyl)silane (**1a**) and results on the pyrolyses of the triphosphanylsilanes (**1a–1c**). Furthermore we report the energy barriers for the decomposition of **1a–1c** to the desired compounds bearing Si–P double and triple bonds and calculations on the relative stabilities of the expected  $RSiP$  isomers **F** and **G**.

## 2. Experimental

### 2.1. General procedures

All manipulations with reagents, synthesis and spectroscopic measurements were carried out under anaerobic conditions in an Ar atmosphere. Solvents were purified by conventional methods and stored under an Ar atmosphere. The starting materials  $Is_2SnF_2$  [12] and  $RSi(PH_2)_3$  ( $R = PH_2$  [13], Me (**1b**), Et (**1c**) [14]) were prepared according to the literature.

### 2.2. Physical measurements

$^1H$ -NMR (250 MHz),  $^{19}F$ -NMR (235.2 MHz),  $^{31}P$ -NMR (101.2 MHz) and  $^{29}Si$ -NMR (99.4 MHz) spectra were recorded in a Bruker DPX 250 and DPX 400 advance spectrometer at room temperature (r.t.) in  $C_6D_6$ . Chemical shifts ( $\delta$ ) are given relative to external standards ( $^1H$ ,  $^{29}Si$ :  $SiMe_4$ ;  $^{31}P$ : 85% aq.  $H_3PO_4$ ;  $^{19}F$ :  $CFCl_3$ ). EI-mass spectra (70 eV) were recorded in a Varian MATCH7 and in a HP GC–MS spectrometer. IR spectra were recorded in a Bruker IFS66 spectrometer.

### 2.3. Synthesis and isolation of fluoro(triphosphanyl)silane (**1a**)

A sample of 6.50 mmol (1.04 g) of  $\text{Si}(\text{PH}_2)_4$  was condensed to a frozen and degassed solution of 6.50 mmol (3.65 g) of  $\text{I}_2\text{SnF}_2$  in ca. 10 ml benzene at  $-196^\circ\text{C}$ . The reaction mixture was allowed to warm up to r.t. and stirred for 48 h.  $^{31}\text{P}$ -NMR monitoring of reaction progress showed that the desired product was formed quantitatively as the only fluoro(phosphanyl)silane derivative. Fractional condensation at r.t. under normal pressure or in vacuo ( $10^{-2}$  torr) into a cooling trap ( $-196^\circ\text{C}$ ) furnished only mixtures of **1a** (max. ca. 60%) and benzene. Isolation of **1a** for in situ crystallization and matrix experiments was achieved by preparative GC under the following conditions: column length: 1 m; diameter: 10 mm; stationary phase: SE 52 with 20% occupancy; column temperature:  $60^\circ\text{C}$ ; injection and detection temperature:  $80^\circ\text{C}$ ; carrier gas: He; flow-rate  $200\text{ ml min}^{-1}$ ; separation volume: 200  $\mu\text{l}$ ; temperature of the trap for collection of **1a**:  $-50^\circ\text{C}$ . Yield from 1 ml of the benzene solution: 5 mg (0.034 mmol). Compound **1a** is a colorless liquid at r.t. and extremely air- and moisture sensitive; m.p. ca.  $-89^\circ\text{C}$ .  $^1\text{H}$ -NMR:  $\delta = 1.77$  (md, PH).  $^{31}\text{P}$ -NMR:  $\delta = -216.1$  (mt,  $^1J(\text{P}, \text{H}) = 188.8$  Hz,  $^2J(\text{P}, \text{P}) = 2.7$  Hz,  $^3J(\text{P}, \text{H}) = 3.8$  Hz,  $^4J(\text{H}, \text{H}) = 0.6$  Hz).  $^{29}\text{Si}$ -NMR:  $\delta = 50.1$  (sep. qd,  $^1J(\text{Si}, \text{F}) = 381.3$  Hz,  $^1J(\text{Si}, \text{P}) = 48.6$  Hz,  $^2J(\text{Si}, \text{H}) = 7.8$  Hz).  $^{19}\text{F}$ -NMR:  $\delta = -142.8$  (sep. q,  $^2J(\text{P}, \text{F}) = 25.9$  Hz,  $^3J(\text{F}, \text{H}) = 9.4$  Hz). EIMS;  $m/z$  (%): 146 ( $[\text{M}]^+$ , 60), 127 ( $[\text{M} - \text{F}]^+$ , 2), 113 ( $[\text{M} - \text{PH}_2]^+$ , 100), 81 ( $\text{SiFPH}_3^+$ , 7), 63 ( $\text{SiPH}_4^+$ , 37), 47 ( $\text{SiF}^+$ , 100). FT-IR (Ar matrix,  $-218^\circ\text{C}$ ) [ $\text{cm}^{-1}$ ]:  $\nu = 2326$  (m), 2318 (s), 2315 (m), 2311 (m), 2311 (m), 2308 (m), 1061 (m), 1057 (m), 856 (s), 853 (vs), 851 (s), 709 (w), 606 (m), 602 (w), 499 (w), 496 (s), 493 (s), 491 (s), 489 (vs), 487 (s), 485 (s); see also Table 1.

### 2.4. X-ray crystal structure analysis of **1a**

A single crystal of **1a** was formed in a capillary tube with a diameter of 0.3 mm on a four-circle diffractometer at 175 K by miniaturized zone melting with focused infra-red radiation [15]. Compound **1a**: formula:  $\text{H}_6\text{FP}_3\text{Si}$ , triclinic, space group  $P\bar{1}$ ,  $a = 6.6194$  (16),  $b = 7.0328$  (16),  $c = 9.042$ (2) Å,  $\alpha = 104.180$ (18),  $\beta = 98.332$ (19),  $\gamma = 117.724$ (16) $^\circ$ ,  $V = 344.62$ (14) Å $^3$ ,  $Z = 2$ ,  $\rho = 1.407\text{ g cm}^{-3}$ ,  $\Theta_{\text{max}} = 32^\circ$ ; of 2834 measured reflections, 2307 were independent ( $R_{\text{merg}} = 0.0328$ ) and 2117 observed ( $I > 2\sigma(I)$ ). The intensities were measured on a Nicolet R3m/V four-circle diffractometer (Mo- $\text{K}\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\omega$  scan,  $T = 123$  K). The structure was solved by direct methods [16], and refined with all measured reflections against  $F^2$  [16]. The fluorine atom F1 and phosphorus atom P1 are disordered over two sites with occupancies 0.5 together

Table 1  
IR spectroscopic data for  $\text{FSi}(\text{PH}_2)_3$  (**1a**)

Argon, 10 K		DFT (B3PW91/6-311G(2d,p))		Assignment <sup>b</sup>	
$\nu$ ( $\text{cm}^{-1}$ )	$I^a$	No.	$\nu$ ( $\text{cm}^{-1}$ )		$I^a$
2326.1	19	27	2400	74	P–H str
2318.3	54	26	2396	27	P–H str
2315.1	6	25	2394	25	P–H str
2311.3	7	24	2387	28	P–H str
2307.7	2	23	2386	19	P–H str
		22	2382	18	P–H str
1060.5	7	21	1095	22	HPH bend
1057.2	41	20	1094	22	HPH bend
		19	1088	14	HPH bend
855.5	10	18	853	100	Si–F str
852.8	73				
850.7	5				
708.9	22	17	716	33	HPH twist
		16	714	38	HPH twist
		15	712	38	HPH twist
498.8	5				
495.6	16				
493.2	27	11	480	70	Si–P str
488.8	100	10	479	70	Si–P str
484.7	14				

<sup>a</sup> Relative intensity based on the strongest peak.

<sup>b</sup> The assignment of the experimental and calculated IR absorption is based on peak position and peak intensities.

with the riding hydrogen atoms H(1A, 1B, 2A, 2B). The Si, P and F atoms were refined anisotropically, and the H atom positions were determined from the difference Fourier maps and refined as riding groups on idealized geometries with the 1.2-fold isotropic displacement parameter of the equivalent  $U_{ij}$  of the corresponding P atom; however the H atoms have little significance due to their disorder character.  $R_1 = 0.0461$ ,  $wR_2 = 0.1177$  (all data), 74 parameter.

### 2.5. Pyrolyses

Flash vacuum pyrolyses (FVP) were carried out by evaporating the sample and passing it through a 7 cm quartz tube which was heated electrically by a tantalum wire. Mass spectra were measured with a VG Quadrupoles SXP Elite spectrometer. The primary ionization energy was usually set to 20 eV for FVP experiments to minimize secondary fragmentations caused by the ion source.

The pulsed deposition unit, built similar to Chen and coworker's [17] and Maier et al.'s [18] description, was described previously [19]. The gas mixtures (500–1000 mbar) were prepared in a 1000 ml glass vessel which was directly connected to the pulse valve. The ratio of the gas mixture (argon/sample) was varied from 1:125 to 1:1000 and the pulse duration from 0.5 to 5 ms (frequency of 1 Hz) in order to optimize the experimental conditions. The temperature of the heating zone



tendency to dismutation under formation of mixed fluoro(phosphanyl)silanes and  $\text{Si}(\text{PH}_2)_4$  (Scheme 4), due to the high stability of the Si–F ( $553 \text{ kJ mol}^{-1}$ ) [28a] versus Si–Cl bond ( $456 \text{ kJ mol}^{-1}$ ) [28b]. **1a** was characterized by means of multi-NMR and IR spectroscopy and mass spectrometry, respectively. Its  $^1\text{H}$ -NMR spectrum shows a doublet of multiplets of higher order at  $\delta = 1.77$ , and the  $^{31}\text{P}$ -NMR spectrum (Fig. 1) a triplet of doublets of a complex multiplet with  $^{29}\text{Si}$ -satellites as expected at high field ( $\delta = -216.1$ ), which represents the M part of a  $[\text{A}_2\text{M}]_3\text{DX}$  spin system ( $\text{X} = ^{29}\text{Si}$ ,  $\text{M} = ^{31}\text{P}$ ,  $\text{A} = ^1\text{H}$ ,  $\text{D} = ^{19}\text{F}$ ). Spectrum simulation of the latter [29] revealed the respective coupling constants (see Ch. 2.3).

The  $^{29}\text{Si}$ -NMR spectrum (Fig. 2) shows, as expected, a septet of a quartet of doublets at  $\delta = 50.1$  with inconspicuous values of  $^1J(\text{Si}, \text{F}) = 381.3 \text{ Hz}$ ,  $^1J(\text{Si}, \text{P}) = 48.6 \text{ Hz}$ , and  $^2J(\text{Si}, \text{H}) = 7.8 \text{ Hz}$ , while its  $^{19}\text{F}$ -NMR spectrum represents a septet of a quartet at  $\delta = -142.8$  with  $^2J(\text{F}, \text{P}) = 25.9$ ,  $^3J(\text{F}, \text{H}) = 9.4 \text{ Hz}$  and  $^{29}\text{Si}$ -satellites (Fig. 3).

The IR spectrum of **1a** was measured in an Ar matrix at 10 K (Fig. 4) and calculated by different levels of theories and basis sets [21–23]. The P–H and Si–P vibrations (Table 1), which were assigned by means of DFT calculations (best agreement with the B3PW91 level of theory) [22e], are almost identical with the values of  $\text{Si}(\text{PH}_2)_4$  [30] and related compounds [31]. The wavenumbers at  $\tilde{\nu} = 851\text{--}856 \text{ cm}^{-1}$  can be assigned to Si–F stretching vibrations and have similar values as those observed for other fluorosilanes (e.g.,  $\text{H}_3\text{SiF}$ :  $\tilde{\nu}(\text{Si–F}) = 892 \text{ cm}^{-1}$ ) [32].

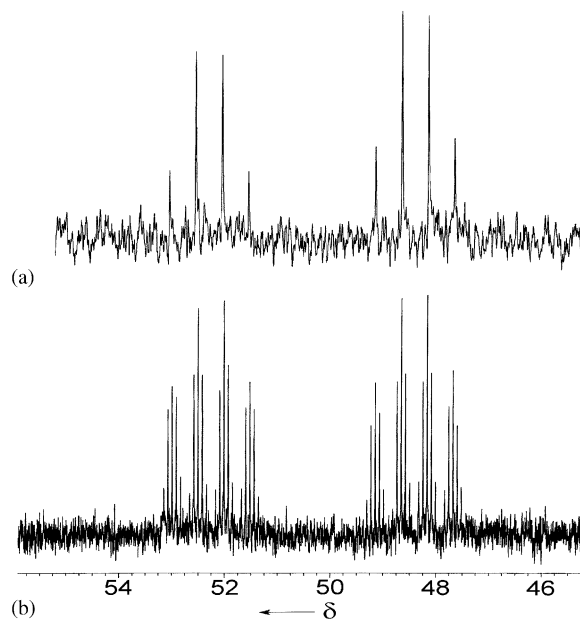


Fig. 2. (a)  $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectrum of **1a**; (b)  $^{29}\text{Si}$ -NMR spectrum of **1a**.

Furthermore, the molecular structure of **1a** was established by a single-crystal X-ray diffraction analysis (Fig. 5). A single crystal was grown in a capillary tube on a four-circle diffractometer at  $-98 \text{ }^\circ\text{C}$  (see Section 2.4). Compound **1a** crystallizes triclinic in the space group  $P\bar{1}$  with two molecules in the unit cell. The F, Si and P atoms are anisotropic, the positions of the H atoms were determined from a difference Fourier map. The F1 and P(1,2) atoms are disordered over two sides with occupancies 0.5 together with the riding H atoms at

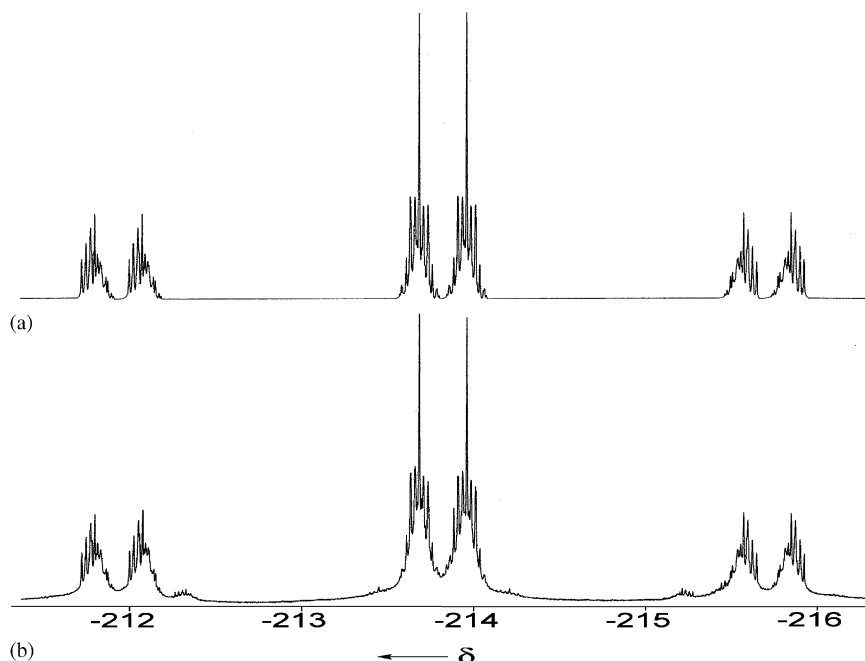
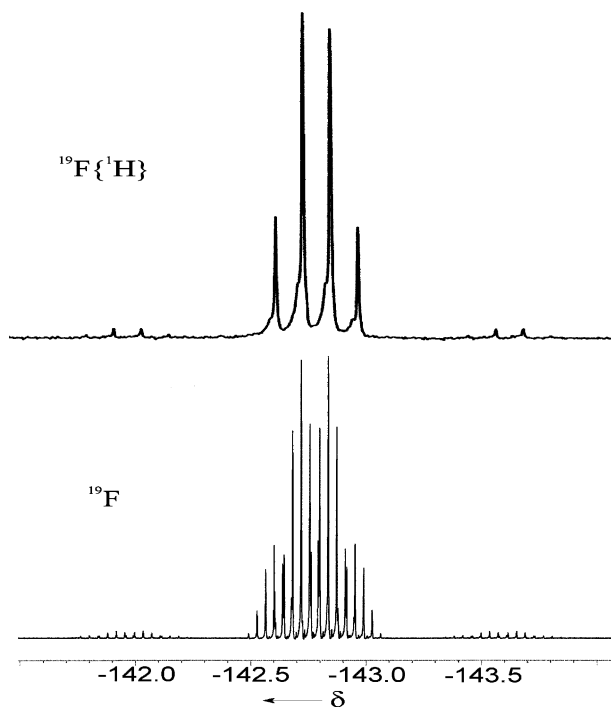
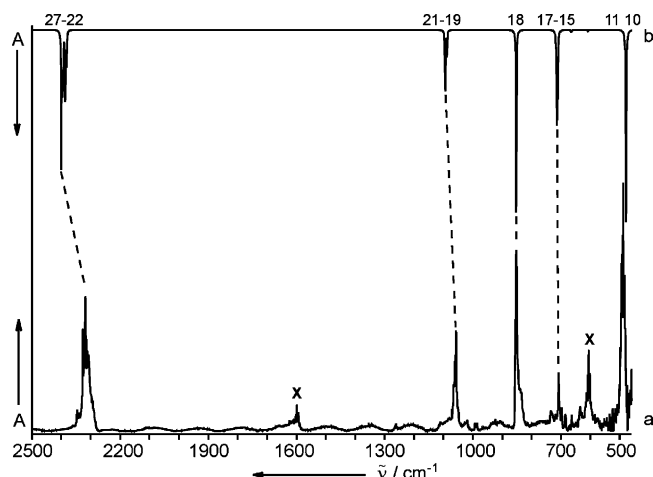


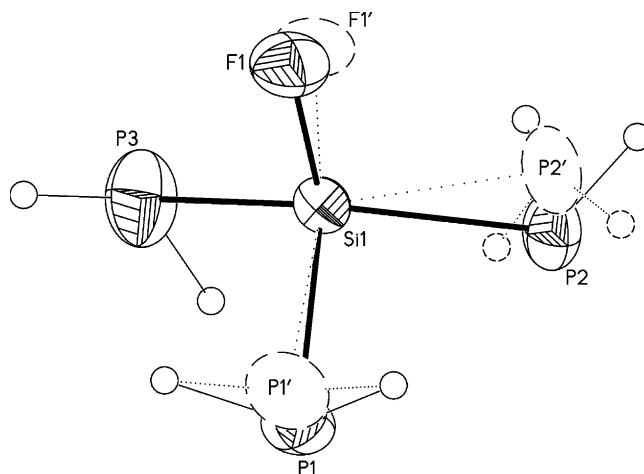
Fig. 1. (a) Simulated and (b) observed  $^{31}\text{P}$ -NMR spectrum of **1a**.



Fig. 3.  $^{19}\text{F}$ -NMR spectra of **1a**.Fig. 4. Bottom (a): IR spectrum (in absorbance) of fluoro(triphosphanyl)silane (**1a**), matrix-isolated in Ar at 10 K. Bands marked with X are due to unidentified impurities. Top (b): IR spectrum of **1a**, calculated at the B3PW91/6-311G(2d,p) level of theory.

phosphorus H(1A, 1B, 2A, 2B). The Si atom is remarkably distorted tetrahedral coordinated with the F1–Si1–P2 angle of  $120.4(7)^\circ$ . The average Si–P distance of  $2.241(2)$  Å is almost identical with that value in  $\text{Si}(\text{PH}_2)_4$  ( $2.240(1)$  Å) [13a], and the Si–F distance of  $1.60(2)$  Å is only marginal different from the values in other fluorosilanes (e.g.  ${}^t\text{Bu}_2\text{Si}(\text{F})\text{OH}$ :  $d(\text{Si}-\text{F}) = 1.57$  Å) [33].

Several *ab initio* and DFT calculations of **1a** were also performed in order to evaluate the influence of different level of theory and basis sets on geometrical parameters.

Fig. 5. Solid state structure of  $\text{FSi}(\text{PH}_2)_3$  **1a**.

Different rotamers of **1a** were taken into consideration but for all theoretical methods only one minimum structure was located. Selected experimental and calculated data are summarized in Table 2. The latter results support that the unusual distortion around the Si atom ( $\text{F}-\text{Si}-\text{P}2$   $120.4(7)^\circ$ ) is not an intrinsic property of the molecule but due to crystal packing forces. It appeared that the most agreement between experimental and calculated geometry and vibrational data (Fig. 4, Table 1) is achieved by using the B3PW91 functional [22e].

#### 4.2. Thermodynamics for the decomposition of $\text{RSi}(\text{PH}_2)_3$ derivatives **1a**, **1b**, **1c**

Thermodynamical data of the decomposition of **1a**, **1b** and **1c** were calculated on the B3LYP/6-311G(2d,p) level of theory to appreciate the applicability of these compounds as suitable precursors for silyldiynes-phosphanes. The reaction enthalpies and Gibbs energies for the formal fragmentation of the investigated  $\text{RSi}(\text{PH}_2)_3$  derivatives into the corresponding Si–P double and triple bond compounds at 298 and 1275 K are summarized in Table 3. The latter temperature corresponds to the lowest thermal conditions of typical pulsed flash pyrolyses [17].

At room temperature all reactions forming multiple bond Si–P systems are calculated to be endothermic, while  $\Delta H_r$  is much larger for the triple bond compounds than for the corresponding silylidene–phosphanes. The thermodynamics of the two organo-substituted derivatives do not show any significant differences, whereas the cleavage of **1a** into two molecules phosphane and  $\text{FSi}\equiv\text{P}$  leads to the highest reaction enthalpy. The Gibbs energies of these reactions are calculated to be also strongly positive indicating that  $\text{RSi}(\text{PH}_2)_3$  seems to be unsuitable for generation of the desired intermediates under normal conditions. While the influence of the temperature on the calculated reaction enthalpies is

Table 2  
Selected experimental and calculated distances (Å) and angles (°) for FSi(PH<sub>2</sub>)<sub>3</sub> (**1a**)

	<i>d</i> (Si–P)	<i>d</i> (Si–F)	F–Si–P	P–Si–P
Experimental	av. 2.241(2)	1.60(2)	110.4(7) [P(1)] 120.4(7) [P(2)] 106.3(1) [P(3)]	102.54(8) [P(1), P(2)] 107.70(7) [P(1), P(3)] 108.91(6) [P(2), P(3)]
MP2/6-31G(d,p)	2.250	1.632	106.4	112.3
MP2/6-311G(2d,p)	2.264	1.614	106.6	112.2
BLYP/6-31G(d,p)	2.303	1.644	105.9	112.8
BLYP/6-311G(2d,p)	2.300	1.638	105.2	113.4
BLYP/cc-pVTZ	2.301	1.646	105.2	113.4
B3LYP/6-31G(d,p)	2.278	1.628	106.0	112.7
B3LYP/6-311G(2d,p)	2.278	1.620	105.6	113.1
B3LYP/6-311G(3df,3pd)	2.269	1.619	105.4	113.2
B3LYP/cc-pVTZ	2.278	1.627	105.4	113.2
B3PW91/6-31G(d,p)	2.266	1.626	106.3	112.5
B3PW91/6-311G(2d,p) <sup>a</sup>	2.264	1.617	105.9	112.8
B3PW91/cc-pVTZ	2.266	1.623	105.8	112.9

<sup>a</sup> Best agreement with experimental data (molecular structure and IR).

Table 3  
Reaction enthalpies and Gibbs energies (in kcal mol<sup>-1</sup>) for the evolution of PH<sub>3</sub> from the triphosphanylsilanes **1a**, **1b** and **1c** calculated at the B3LYP/6-311G(2d,p) level of theory

	$\Delta H_r$		$\Delta G_r$	
	298 K	1275 K	298 K	1275 K
<i>cis</i> -F(PH <sub>2</sub> )Si=PH	31.72	28.06	21.62	-8.44
<i>trans</i> -F(PH <sub>2</sub> )Si=PH	32.29	28.67	22.17	-8.03
FSi≡P	80.60 <sup>a</sup>	73.95 <sup>a</sup>	61.09 <sup>a</sup>	2.69 <sup>a</sup>
<i>cis</i> -Me(PH <sub>2</sub> )Si=PH	29.83	26.22	19.30	-12.23
<i>trans</i> -Me(PH <sub>2</sub> )Si=PH	30.26	26.67	19.75	-11.76
MeSi≡P	67.84 <sup>a</sup>	60.29 <sup>a</sup>	47.29 <sup>a</sup>	-13.74 <sup>a</sup>
<i>cis</i> -Et(PH <sub>2</sub> )Si=PH	29.55	25.90	18.92	-12.90
<i>trans</i> -Et(PH <sub>2</sub> )Si=PH	29.99	26.34	19.50	-11.84
EtSi≡P	66.82 <sup>a</sup>	59.23 <sup>a</sup>	46.21 <sup>a</sup>	-15.00 <sup>a</sup>

<sup>a</sup> Cleavage of two molecules PH<sub>3</sub>.

negligibly small, the values of  $\Delta G_r$  decrease strongly, especially for the silyldiyne–phosphanes, at 1275 K, and the reactions are predicted to be even exergonic. Only the generation of FSi≡P is still slightly endergonic, but is expected to become also negative at temperatures above 1000 °C. Accordingly, from the thermodynamical viewpoint the Si–P multiple bond intermediates should be accessible from the precursors **1a**, **1b** and **1c** at high temperatures.

#### 4.3. Relative energies of RSiP isomers

The structures and relative energies of the isomers **F**, **G** and the corresponding transition states with fluoro, methyl, ethyl and further substituents are calculated using B3LYP/6-311G(2d,p)+ZPE theory. The received results are in good agreement with calculations on the

RSiP potential surface (R = first row substituents) by Lai et al. [34]. Linear geometries are located for all RSiP derivatives with Si≡P triple bonds showing only very slight differences in their bond length (1.961 ± 0.005 Å). However, the isomeric silyldiyne–phosphylidenes are predicted to be nonlinear and differ strongly in their geometrical parameters depending on the substituent R (Fig. 6). For instance, SiPF shows a bridged structure with a Si–P distance of 2.124 Å and a Si–P–F angle of 54.2°, whereas the phenyl substituted species is calculated to have values of 2.056 Å and 128.6° and thus clearly possesses Si–P double bond character.

In accordance with theoretical results of RSi≡N isomers [8] the relative stabilities of **F** versus **G** roughly correlate with the electronegativity of substituent R (Table 4). The parent system was already investigated on the MP3/6-31G(d)//RHF/3-21G(d) and G2 level of theory, and the hydrogen-bridged isomer was found to be more stable by 9.4 and 10.4 kcal mol<sup>-1</sup> than the HSi≡P triple bond species, respectively [9].

The DFT calculations are in nice agreement with the previous values and predict a further stabilization of **G** relative to **F** if hydrogen is replaced by a  $\sigma$ -donor substituent like SiH<sub>3</sub>. Organic groups on the SiP moiety lead to a slight energetically advantage of the linear structure, even MeSi≡P is 4.6 kcal mol<sup>-1</sup> lower in energy than its isomer. As expected, the experimentally desired fluoro and methoxy substituted silyldiyne–phosphanes are calculated to be the most stable compounds by -21.7 and -22.9 kcal mol<sup>-1</sup> relative to their isomers reflecting the stronger dissociation energies of Si–F and Si–O bonds, respectively. However, the stability of RSiP strongly decreases for R = Cl and Br resulting in approximately identical energies of **F** and **G** for the latter substituent. Surprisingly, the non-

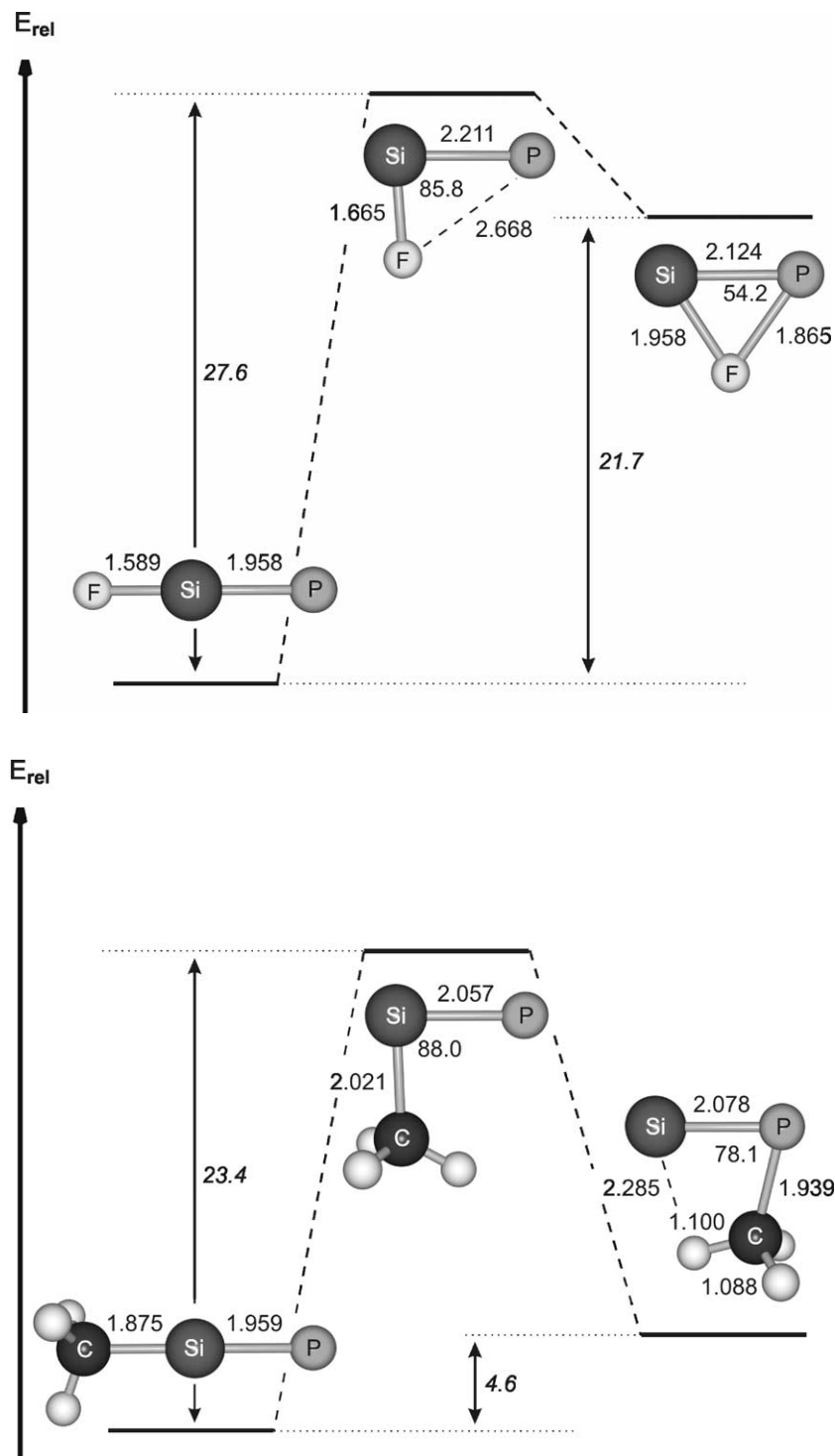


Fig. 6. Schematic presentation of energy profiles and structures for FSiP and CH<sub>3</sub>SiP isomers (F, TS and G) calculated at the B3LYP/6-311G(2d,p) level of theory. Bond lengths and angles are given in Å and degrees, respectively. Relative energies in kcal mol<sup>-1</sup>.

linear Si–P double bond compound is energetically favored for the electron withdrawing group CF<sub>3</sub>. This effect can be explained by the elongated in-plane C–F bond (1.44 Å) and the short Si–F distance (2.27 Å) of

the bridged structure which clearly indicate stabilizing interactions between these two atoms.

The calculated isomerization barriers show the largest relative energies for R = F and OCH<sub>3</sub> (27.6 and 32.6



Table 4

Relative energies (in kcal mol<sup>-1</sup>) of RSi≡P (taken as zero) and :SiPR isomers ( $\Delta E$ ) plus corresponding transition states ( $\Delta E_a$ ) calculated at the B3LYP/6-311G(2d,p) level of theory including zero point energy ZPE

	R	$\Delta E$	$\Delta E_a$
a	H	-11.8	11.0
b	CH <sub>3</sub>	4.6	23.4
c	C <sub>2</sub> H <sub>5</sub>	2.4	22.1
d	C <sub>3</sub> H <sub>7</sub>	2.1	22.1
e	Ph	3.7	20.5
g	CF <sub>3</sub>	-9.9	16.0
h	OCH <sub>3</sub>	22.9	32.6
i	F	21.7	27.6
j	Cl	4.8	19.7
k	Br	0.3	16.9
l	SiH <sub>3</sub>	-14.7	7.4

kcal mol<sup>-1</sup>). Therefore the electronically stabilized FSi≡P and H<sub>3</sub>COSi≡P should be excellent candidates for synthesis and characterization of Si≡P triple bond species.

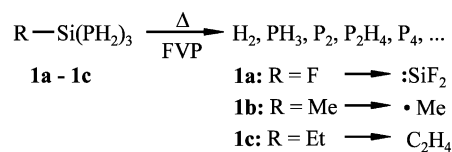
#### 4.4. Flash vacuum and pulsed pyrolyses

The thermal decay of precursors **1a**, **1b** and **1c** was at first experimentally investigated by flash vacuum pyrolysis (FVP) with mass spectroscopic identification of the products. At temperatures between 400 and 600 °C all three educts decompose almost completely. This was monitored by the strongly decreasing molecule ion peaks. Simultaneously, for ethyl-(triphosphanyl)silane (**1c**) new intense fragments at  $m/e = 2, 28, 34$  and  $62$  are growing in which can be undoubtedly assigned to hydrogen, ethane, phosphane and P<sub>2</sub>, respectively (Fig.

7). Additionally, diphosphane ( $m/e = 66$ ) and P<sub>4</sub> ( $m/e = 124$ ) are detected as minor products. If the same pyrolyses are performed with matrix-IR coupling the obtained spectra agree excellently with the results from mass spectroscopy.

Thermolyses of the compounds **1a** and **1b** result basically in the formation of the same products. For the methyl-substituted precursor traces of methyl radicals are observed at the highest temperature instead of ethane, while the fluoro derivative decomposes additionally into difluorosilylene (Scheme 5).

However, the FVP experiments of **1a**, **1b** and **1c** do not provide any direct evidence for the generation of the desired reactive intermediates, but clearly indicate that these precursors thermally split off phosphanes, especially PH<sub>3</sub>, which is known to decompose into H<sub>2</sub>, P<sub>2</sub> and P<sub>4</sub> on quartz surfaces above temperatures of 400 °C [35]. Under the described experimental conditions labile species with Si–P multiple bonds are either not formed or too short-lived for their spectroscopic identification. Furthermore, the thermolysis of the three triphosphanyl silane derivatives was investigated by using the pulsed pyrolysis technique with matrix-IR coupling. The main differences compared to FVP are shorter contact times of the precursor molecules due to near-sonic flow velocities through the length of the pyrolysis tube and cooling of the products in the postpyrolysis



Scheme 5. Products from flash-vacuum pyrolysis of **1a–1c**.

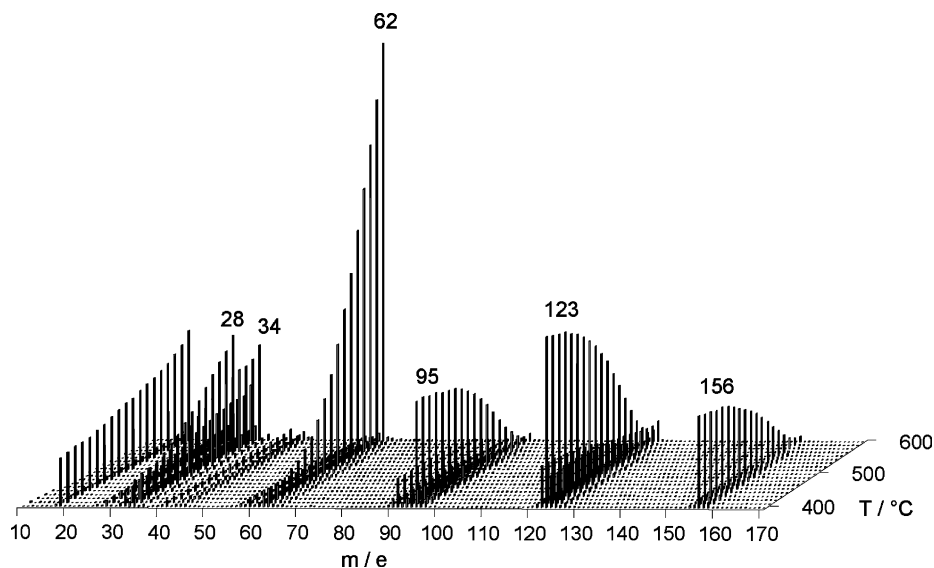


Fig. 7. spectrometric analysis of the fragments generated by FVP of ethyl(triphosphanyl)silane (**1c**) depending on the temperature (400–600 °C). The growing peaks at  $m/e = 28, 34$  and  $62$  indicate the formation of C<sub>2</sub>H<sub>4</sub>, PH<sub>3</sub> and P<sub>2</sub>, respectively.

supersonic jet expansion [17]. Additionally, the thermal energy is transferred by collisions with hot inert gas molecules to the precursor, and thus secondary reactions and wall effects are diminished. Under these experimental conditions **1c** decomposes almost quantitatively at temperatures above 1200 °C. The absorptions in the product IR spectrum are assigned as ethane, phosphane and traces of silicon monoxide, and thus the ethyl-substituted precursor seems to be subject to the same thermolytic decay as in the FVP experiments.

Pulsed pyrolyses of fluoro(triphosphanyl)silane **1a** lead to its complete thermal decomposition at temperatures above 1100 °C resulting in a set of new IR bands (Fig. 8).

By comparison with IR data of the literature the main absorptions can be assigned to SiF<sub>4</sub>, SiF<sub>2</sub>, SiO and HF. However, HF was not detected in FVP experiments of **1a**.

Additionally the spectrum shows small amounts of PH<sub>3</sub> and Si<sub>2</sub>O<sub>2</sub>. However, the two intense bands at 989 and 772 cm<sup>-1</sup>, whose corresponding products are thermally and photochemically stable under matrix isolation conditions, remain hitherto unassigned. According to band position and intensity the former is in good agreement with the calculated Si–F stretching vibration of FSi≡P on the B3LYP/6-311G(2d,p) level of theory, but do probably not belong to a reactive intermediate since the same absorption is also observed after depositing samples of **1a** without pyrolysis which were allowed to stand overnight. Although the products generated by pulsed pyrolysis of **1a** partly differ from the results of FVP experiments, once again no evidence is found relating to the desired reactive intermediates. In

contrast to **1a**, the methyl-substituted derivative **1b** does not decompose quantitatively by pulsed pyrolysis even at the highest temperature of 1400 °C. Apart from the bands of **1b** a typical IR spectrum shows PH<sub>3</sub>, SiO and CH<sub>4</sub> as main products, and additionally intense absorptions in the region of 950–850 and 750–650 cm<sup>-1</sup>, respectively. Smaller bands at 2150 and 1935 cm<sup>-1</sup> indicate that probably molecules containing Si–H bonds are formed during the process of thermolysis. All products of the pulsed pyrolysis are photochemically stable, while a set of IR-absorptions (1935, 1439, 730–680 cm<sup>-1</sup>) strongly decreases after warming up the matrix to 38 K for several hours. Thus, contrary to the findings for **1a** and **1c** reactive intermediates might be generated. If the experimental absorptions are compared with calculated spectra (B3LYP/6-311G(d,p)) of potential candidates, the formation of most species, especially CH<sub>3</sub>Si≡P and HSi≡P, cannot be ruled out, but also the data do not allow definite assignments.

#### 4.5. Conclusions

We prepared and isolated the first fluorophosphanylsilane **1a** which is stable with regard to F/PH<sub>2</sub> dismutation processes. Although theoretical investigations suggest that triphosphanylsilanes could be versatile precursors for the synthesis of unsaturated Si–P compounds, neither **1a** nor the alkylsubstituted derivatives **1b**, **c** are suitable for the formation of a silyldiynephosphane or other unsaturated Si–P compounds under FVP or pulsed pyrolyses and matrix isolation conditions. The decomposition experiments under controlled thermal conditions suggest that the Si–P containing

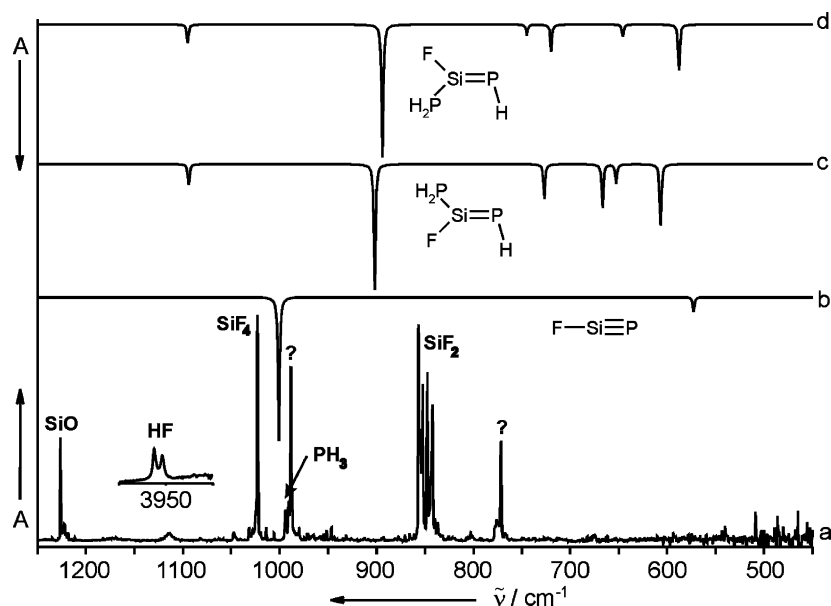


Fig. 8. (a) IR spectrum of the products generated by pulsed pyrolysis ( $\sim 1100$  °C) of fluoro(triphosphanyl)silane (**1a**), matrix-isolated in Ar at 10 K; (b) IR spectrum of fluorosilyldiynephosphane, calculated with B3LYP/6-311G(2d,p); (c) calculated IR spectrum of the corresponding *trans*-silyldiynephosphane; (d) calculated IR spectrum of the *cis*-isomer.

products, if they are formed, are highly reactive intermediates which may undergo conversion on the glass wall to SiO and SiF<sub>2</sub>. Apparently, alternative precursors are necessary in order to synthesis a silyldiyne–phosphane RSi≡P with R = Cl or F at silicon under less drastic thermal decomposition conditions. Corresponding investigations for the synthesis of other suitable Si–P precursors are in progress.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Fachinformationszentrum Karlsruhe, CSD no. 413092. Copies of this information may be obtained free of charge from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808666; e-mail: crysdata@fiz-karlsruhe.de).

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## References

- [1] (a) Comprehensive reviews on Si=E compounds, Si=C: A.G. Brook, M.A. Brook, *Adv. Organomet. Chem.* 39 (1996) 71; (b) Si=N: I Hemme, U. Klingebiel, *Adv. Organomet. Chem.* 39 (1996) 159; (c) Si=P, Si=As: M. Driess, *Adv. Organomet. Chem.* 39 (1996) 193; (d) M. Driess, *Coord. Chem. Rev.* 145 (1995) 1; (e) G. Fritz, P. Scheer, *Chem. Rev.* 100 (2000) 3341; (f) Si=Si: R. Okazaki, R. West, *Adv. Organomet. Chem.* 39 (1996) 232; (g) T. Müller, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 68; (h) J. Escudie, H. Ranaivonjatovo, L. Rigon, *Chem. Rev.* 100 (2000) 3639.
- [2] (a) M. Driess, S. Rell, H. Pritzkow, *J. Chem. Soc. Chem. Commun.* (1995) 253.; (b) M. Driess, S. Rell, R. Janoschek, H. Pritzkow, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1326; (c) M. Driess, S. Rell, K. Merz, *Z. Anorg. Allg. Chem.* 625 (1999) 1119.
- [3] P. Jutzi, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 3797.
- [4] (a) R.S. Grev, *Adv. Organomet. Chem.* 33 (1991) 125; (b) H. Jacobsen, T. Ziegler, *J. Am. Chem. Soc.* 116 (1994) 3667; (c) H. Lischka, H.J. Kohler, *J. Am. Chem. Soc.* 105 (1983) 6646.
- [5] M. Bogey, H. Bolvin, C. Demyneck, J.L. Destombes, *Phys. Rev. Lett.* 66 (1991) 413.
- [6] M. Karni, Y. Apeloig, D. Schröder, W. Zummack, R. Rabezzana, H. Schwarz, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 332.
- [7] N. Wiberg, W. Niedermayer, G. Fischer, H. Nöth, M. Suter, *Eur. J. Inorg. Chem.* (2002) 1066.
- [8] Y. Apeloig, K. Albrecht, *J. Am. Chem. Soc.* 117 (1995) 7263.
- [9] (a) K.J. Dykema, T.J. Troung, M.S. Gordon, *J. Am. Chem. Soc.* 107 (1985) 4535; (b) A.G. Baboul, H.B. Schlegel, *J. Am. Chem. Soc.* 118 (1996) 8444.
- [10] (a) G. Maier, J. Glatthaar, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 473; (b) J.F. Ogilvie, S. Craddock, *J. Chem. Soc. Chem. Commun.* (1966) 346.; (c) J.G. Radziszewski, D. Littmann, V. Balaji, L. Fabry, G. Gross, J. Michl, *Organometallics* 12 (1993) 4816.
- [11] H. Bock, R. Dammel, *Angew. Chem. Int. Ed. Engl.* 24 (1985) 111.
- [12] G. Anselme, H. Ranaivonjatovo, J. Escudie, C. Couret, J. Satgé, *Organometallics* 11 (1992) 2748.
- [13] (a) M. Driess, C. Monsé, R. Boese, D. Bläser, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 2257; (b) M. Driess, C. Monsé, K. Merz, *Z. Anorg. Allg. Chem.* 627 (2001) 1225.
- [14] M. Baudler, G. Scholz, W. Oehlert, *Z. Naturforsch. Teil b* 44 (1989) 627.
- [15] R. Boese, M. Nussbaumer, in: D.W. Jones (Ed.), *In Situ Crystallisation Techniques in Organic Crystal Chemistry*, Oxford University Press, Oxford, UK, 1994, pp. 20–37.
- [16] G.M. Sheldrick, SHELXL-97, Universität Göttingen, Germany, 1997.
- [17] (a) D.W. Kohn, H. Clauberg, P. Chen, *Rev. Sci. Instrum.* 63 (1992) 4003; (b) J.A. Blush, H. Clauberg, D.W. Kohn, D.W. Minsek, X. Zhang, P. Chen, *Acc. Chem. Res.* 25 (1992) 385.
- [18] G. Maier, T. Preiss, H.P. Reisenauer, *Chem. Ber.* 127 (1994) 779.
- [19] M. Halupka, W. Sander, *Spectrochim. Acta Part A* 54 (1998) 495.
- [20] W. Sander, G. Bucher, S. Wierlacher, *Chem. Rev.* 93 (1993) 1583.
- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, *GAUSSIAN-98*, Revision A.9, Pittsburgh, PA, 1998.
- [22] (a) MP2: C. Möller, M.S. Plesset, *Phys. Rev.* 46 (1934) 618; (b) BLYP: A. Becke, *Phys. Rev. A* 38 (1988) 3098; (c) C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785; (d) B3LYP: A. Becke, *J. Chem. Phys.* 98 (1993) 5648; (e) B3PW91: J.P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B* 54 (1996) 16533.
- [23] (a) R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, *J. Chem. Phys.* 72 (1980) 650; (b) T.H. Dunning, *J. Chem. Phys.* 90 (1989) 1007; (c) R.A. Kendall, T.H. Dunning, R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6796; (d) D.E. Woon, T.H. Dunning, *J. Chem. Phys.* 98 (1993) 1358.
- [24] A.D. Norman, D.C. Wingleth, *Inorg. Chem.* 9 (1970) 98.
- [25] (a) E.G. Teach, A.J. Leffler, *J. Am. Chem. Soc.* 82 (1960) 2710; (b) H. Albers, R. Schuler, *Chem. Ber.* 79 (1943) 23; (c) A.E. Finholt, C. Helling, V. Imhof, L. Nielsen, E. Jacobsen, *Inorg. Chem.* 2 (1963) 504; (d) M. Driess, K. Merz, H. Pritzkow, R. Janoschek, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 2507.
- [26] (a) G. Fritz, H. Schäfer, *Z. Anorg. Allg. Chem.* 407 (1974) 295; (b) G. Fritz, H. Schäfer, R. Demuth, J. Grobe, *Z. Anorg. Allg. Chem.* 407 (1974) 287.

- [27] M. Driess, C. Monsé, K. Merz, *Chem. Commun.* (2003) in press.
- [28a] M. Farber, R.D. Srivastava, *J. Chem. Soc. Faraday Trans.* 74 (1978) 1089.
- [28b] V.N. Kondratiev, *Bond Dissociation Energies, Ionisation Potentials and Electron Affinities*, Mauka Publishing House, Moscow, 1974.
- [29] The spectrum simulation was carried out with the program PERCH, Version 1/96, University of Kuopio (Finland).
- [30] C. Monsé, Ph.D. Thesis, Ruhr-University Bochum, 2000.
- [31] (a) J.A. Lannon, E.R. Nixon, *Spectrochim. Acta Part A* 23 (1967) 2713;  
(b) J.E. Drake, C. Riddle, *Spectrochim. Acta Part A* 26 (1970) 1697.
- [32] D.F. Ball, M.J. Buttler, D.C. McKean, *Spectrochim. Acta* 21 (1965) 451.
- [33] N.H. Buttrus, C. Eaborn, P.B. Hitchcock, A.K. Saxena, *J. Organomet. Chem.* 287 (1985) 157.
- [34] C.H. Lai, M.D. Su, S.Y. Chu, *Inorg. Chem.* 41 (2002) 1320.
- [35] V.S. Bans, M. Etnenberg, *J. Phys. Chem. Solids* 34 (1973) 1119.