ELSEVIER

Synthesis and structural characterization of carbon-centered tris(pentafluorophenyl)silyl derivatives

Alexander D. Dilman [a,*], Dmitry E. Arkhipov [b], Alexander A. Korlyukov [*,c],
Valentine P. Ananikov [a], Vitalij M. Danilenko [b], Vladimir A. Tartakovsky [a]

[a] N. D. Zelinsky Institute of Organic Chemistry, 119991 Moscow, Leninsky prosp. 47, Russian Federation
[b] Moscow Chemical Lyceum, 109033 Moscow, Tamozhennyi pr. 4, Russian Federation
[c] A. N. Nesmeyanov Institute of Organoelement Compounds, 119991 Moscow, Vavilov str. 28, Russian Federation

Abstract

A general method for the synthesis of carbon-centered tris(pentafluorophenyl)silyl derivatives ($RSi(C_6F_5)_3$) by reaction of trichlorosilanes ($RSiCl_3$) with pentafluorophenylmagnesium bromide was described. The crystal structures of obtained compounds were studied by X-ray diffraction analysis (7 structures). The peculiarities of crystal packing were analyzed by means of DFT calculations.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Organosilicon compounds bearing at the silicon atom three heteroatomic substituents ($RSiX_3$, X = Hal, OR′) have found widespread use in organometallic chemistry [1], in materials science [2], and as reagents in organic synthesis [3]. The key feature of these derivatives corresponds to their facile associative interaction with nucleophiles affording species with hyper-coordinate silicon [4]. Even week nucleophiles such as dimethyl ether may form five-coordinate complex with trichlorosilane [5]. Similarly, trichloro- and trialkoxysilanes easily undergo hydrolysis reaction, which likely proceeds through five- or six-valent intermediates [6]. At the same time, it would be interesting to consider compounds bearing at the silicon atom three electron withdrawing carbon centered groups. It may be expected that owing to significant differences in the nature of silicon-heteroatom and silicon–carbon bonds, in the latter case new reactivity patterns may emerge.

Among many electron acceptors the pentafluorophenyl group is particularly attractive, since its ability for the modification of Lewis acidic or basic properties of different elements has been noted and extensively exploited [7]. In addition, pentafluorophenyl organometallic reagents are easily accessible and, contrary to many other fluorinated carbanions, quite stable [8]. Accordingly, we decided to synthesize tris(pentafluorophenyl)silyl (TPFS) derivatives and investigate their structural characteristics.

Several representatives of this class have been described in the literature [9], but no general approach for their synthesis has been proposed. Herein, we present a convenient procedure for the preparation of various compounds containing TPFS group and discuss on their structures studied by X-ray diffraction analysis.

* Corresponding author. Tel.: +7 095 938 35 60; fax +7 095 135 53 28.
E-mail addresses: adil25@mail.ru (A.D. Dilman), alex@xrlab.ineos.ac.ru (A.A. Korlyukov).

2. Results and discussion

2.1. Synthesis of TPFS derivatives

For the preparation of TPFS group, we selected the approach involving coupling of trichlorosilanes with three molecules of pentafluorophenyl carbanion. From practical point of view, the most convenient way to the pentafluorophenyl nucleophile consists of formation of Grignard reagent directly from bromopentafluorobenzene and magnesium in diethyl ether [8a]. Surprisingly, when the obtained dark brown solution was combined with organotrichlorosilane **1** no reaction was observed. However, subsequent addition of tetrahydrofuran in the amount equal to that of ether caused rapid reaction as evidenced by the precipitation of magnesium salts. Presumably, significant rate acceleration exhibited by tetrahydrofuran may be connected with better solvation of magnesium leading to the deaggregation of organomagnesium reagent. Employment of ether/tetrahydrofuran solvent system allows for the preparation of various TPFS derivatives (Scheme 1, Table 1). Silanes containing synthetically valuable functionalities such as allyl, benzyl, phenyl, vinyl, and alkynyl can be readily synthesized as stable and distillable compounds.

Despite steric bulkiness created in the resulting TPFS fragment, the introduction of three pentafluorophenyl groups proceeds quite easily [10]. It is believed that after the introduction of pentafluorophenyl group the remaining chlorines become more reactive than in the parent trichlorosilane [11].

The present method is advantageous in comparison with the approach employing organolithium reagent. Thus, compounds **2h** [9a,12] and **2j** [9b] were previously prepared from corresponding trichlorosilanes and pentafluorophenyllithium in 67% and 38% yield, respectively, while as shown in Table 1 (entries 8 and 10), yields of 75% and 68% can be achieved using our approach. Furthermore, the procedure reported herein is easier to perform and can be applied to larger scale syntheses, as tested for the preparation of 80 g of **2h** in a single run.

It should be pointed out that compounds **2a–k** are absolutely insensitive towards water, thus allowing for very convenient handling and storage. Moreover, aqueous work-up can be employed upon their isolation. The inertness of carbon-centered TPFS derivatives stands in sharp contrast with the behavior of oxygen-centered counterparts, $ROSi(C_6F_5)_3$, which are moisture sensitive [13].
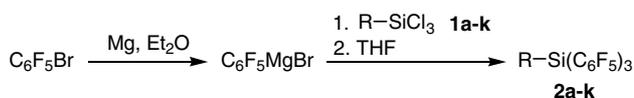
Table 1
Synthesis of TPFS derivatives[a]

Entry	1		2	Yield of **2**, %[b]
1	$Me{-}SiCl_3$	**1a**	**2a**	74
2	$Cl{\diagdown}SiCl_3$	**1b**	**2b**	67
3	$Cl{\diagdown\diagdown}SiCl_3$	**1c**	**2c**	85
4	$SiCl_3$ (allyl)	**1d**	**2d**	93
5	$SiCl_3$ (methallyl)	**1e**	**2e**	85
6	$Ph{\diagdown}SiCl_3$	**1f**	**2f**	65
7	$Ph{\diagdown}SiCl_3$ with Me	**1g**	**2g**	70
8	$Ph{-}SiCl_3$	**1h**	**2h**	75
9	$SiCl_3$ (vinyl)	**1i**	**2i**	72
10	$Ph{\diagup}SiCl_3$	**1j**	**2j**	68
11	$Ph{-}{\equiv}{-}SiCl_3$	**1k**	**2k**	67

[a] The ratio **1**:Mg:C_6F_5Br = 1:3.1:3.1.
[b] Isolated yield.

2.2. Structural studies

To date only one carbon-centered TPFS derivative, namely $(C_6F_5)_4Si$, has been structurally characterized [14]. In this regard, the examination of the series of compounds differing only in the organic substituent (R) is expected to provide meaningful information on the properties of the TPSF group in the solid state.

The crystal and molecular structures of **2a**, **b**, **d**, **f**, **g**, **i**, **k** were investigated by X-ray diffraction analysis (Figs. 1–7 and Tables 2 and 3). The presence of fluorine atoms in all *ortho* positions of phenyl rings of **2** imparts significant steric bulk to the TPFS fragment that is reflected in the crystal structures. For example, in compounds **2a**, **b**, **d**, **f**, **g** where TPFS group is attached to sp³ carbon, the
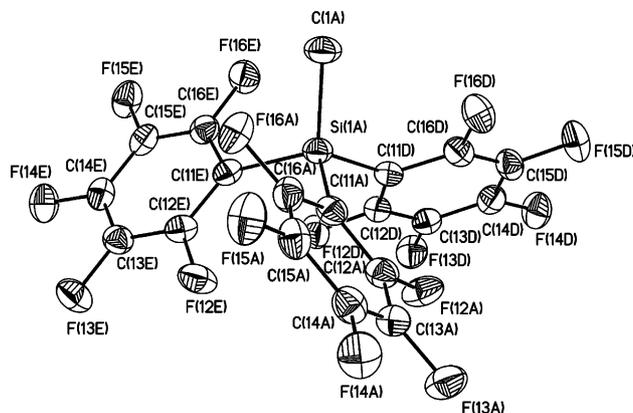

Fig. 1. Molecular structure of one of three independent molecules **2a** presented by thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. CCDC 262523.
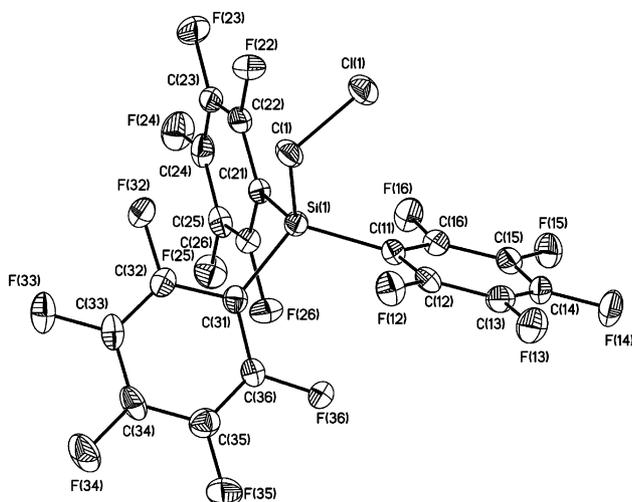

$$C_6F_5Br \xrightarrow{\text{Mg, Et}_2O} C_6F_5MgBr \xrightarrow[\text{2. THF}]{\text{1. R}{-}SiCl_3 \;\; \mathbf{1a\text{-}k}} R{-}Si(C_6F_5)_3$$
$$\mathbf{2a\text{-}k}$$

Scheme 1.

Fig. 2. Molecular structure of **2b** presented by thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. CCDC 262524.

Fig. 5. Molecular structure of **2g** presented by thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. CCDC 262527.
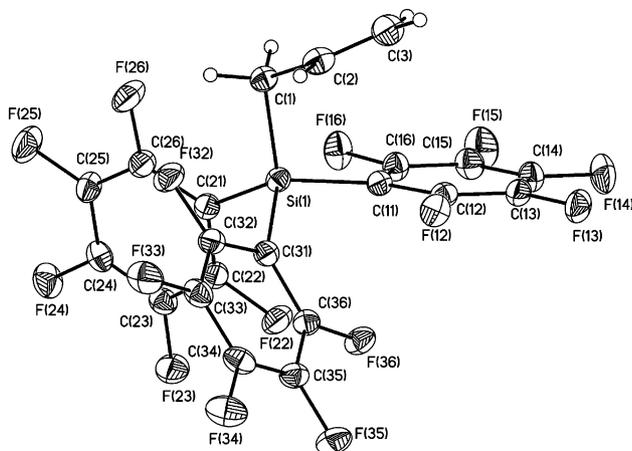

Fig. 3. Molecular structure of **2d** presented by thermal ellipsoids at 50% probability. CCDC 262525.
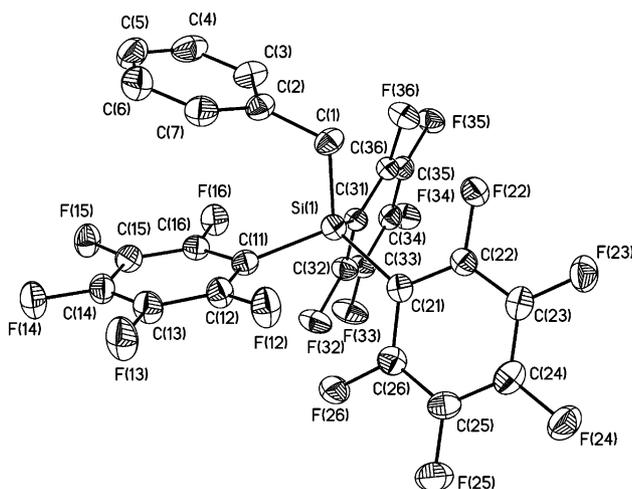

Fig. 6. Molecular structure of **2i** presented by thermal ellipsoids at 50% probability. CCDC 262528.

Fig. 4. Molecular structure of **2f** presented by thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. CCDC 262526.
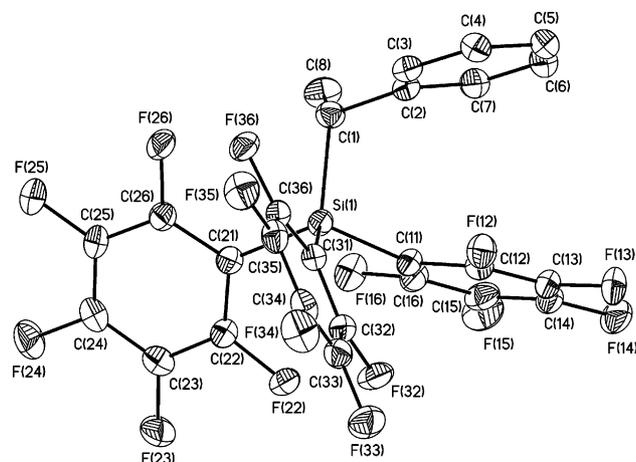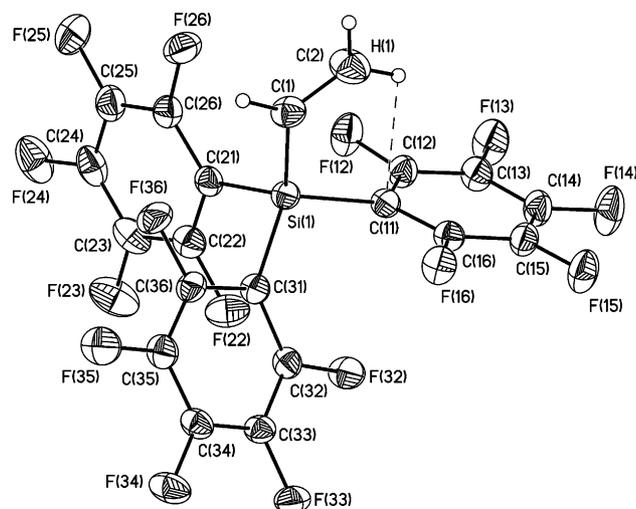
bond distance C_{sp^3}–Si_{TPFS} increases with the increase of steric requirements of the substituent, from 1.856 Å in **2a** (R = Me) to 1.887 Å in **2g** (R = α-phenylethyl). On the other hand, the electron withdrawing influence of three pentafluorophenyl groups tends to reduce the bond length between TPFS moiety and adjacent carbon atom. Thus, in compound **2k** (R = PhC≡C) the distance C_{sp}–Si_{TPFS} of 1.798 Å was observed, which is shorter than typical values of 1.82–1.85 Å for silyl alkynes (analysis of 178 structures from Cambridge data base). Similar phenomenon has recently been encountered for oxygen-centered TPFS derivatives, ROTPFS, that exhibited the shortest oxygen–silicon bond lengths [13]. However, the distances between carbon and silicon in **2a**, **b**, **d**, **f**, **g**, **i** lie within the typical range suggesting that the extent of bond reduction depends on the nature of substituent.
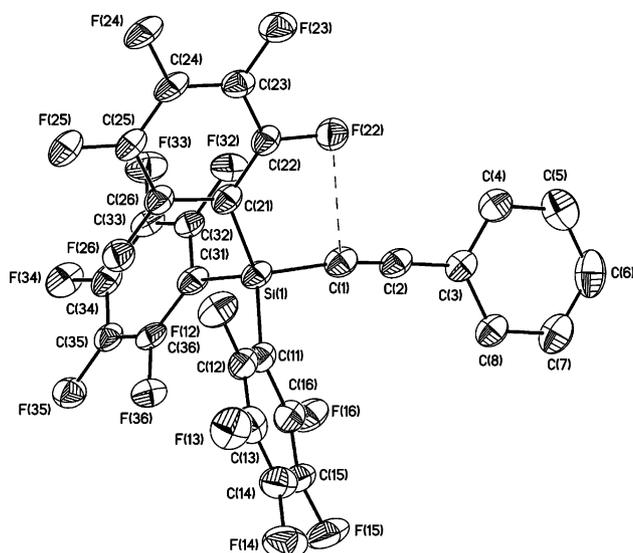
Fig. 7. Molecular structure of **2k** presented by thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. CCDC 262529.

The silicon atom in **2** has slightly distorted tetrahedral geometry. In the structure of **2a** the configuration of silicon is almost ideal tetrahedral while in compounds with more bulky groups such as benzyl (**2f**) or α-phenylethyl (**2g**) the distortion of tetrahedral configuration becomes noticeable with the C–Si–C angles ranging from 103° to 114° (Table 3).

Concerning carbon atoms, of particular note is the bending of silylacetylene fragment in compound **2k** with the angle Si–C≡C of 171.04°. Such deviation results in close contact between an acetylene carbon and a fluorine atoms, C···F 2.94 Å (Fig. 7).

Relative position of the organic substituent (R) at silicon and perfluorinated phenyl rings deserves special comments. In most of studied compounds the substituent and one C_6F_5 group are in distorted *gauche* conformation (torsion angles vary from 38.5° to 71.2°). The only exception is **2i** (R = vinyl) where the relative positions of vinyl with respect to C_6F_5 ring may be described as eclipsed (angle C(11)Si(1)C(1)C(2) = 3.24°). Such conformation results in proximate arrangement of C(11)···H(1), 2.73 Å, that may be regarded as weak intramolecular C–H···pi interaction [15,16]. In the structure of **2f** (R = $PhCH_2$), the interplanar angle between planes of phenyl and one pentafluorophenyl groups is 21.2° with the interatomic distance C(2)···C(11) being equal to 3.066 Å. In addition, the

Table 2
Crystallographic parameters of studied compounds

	2a	2b	2d	2f	2g	2i	2k
Molecular formula	$C_{19}H_3F_{15}Si$	$C_{19}H_2ClF_{15}Si$	$C_{21}H_5F_{15}Si$	$C_{25}H_7F_{15}Si$	$C_{26}H_9F_5Si$	$C_{20}H_3F_{15}Si$	$C_{26}H_5F_{15}Si$
Formula weight	544.30	578.75	570.34	620.40	634.42	556.31	630.39
Melting point (°C)	89–90	119–122	48–51	133–141	182–188	117–119	170–175
Dimension (mm)	$0.2 \times 0.2 \times 0.2$	$0.3 \times 0.2 \times 0.03$	$0.2 \times 0.1 \times 0.1$	$0.3 \times 0.3 \times 0.3$	$0.1 \times 0.07 \times 0.02$	$0.3 \times 0.2 \times 0.08$	$0.1 \times 0.1 \times 0.02$
Crystal system	Trigonal	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P3$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions							
a (Å)	15.5358(17)	9.8335(17)	7.3223(5)	7.348(3)	11.159(3)	16.196(7)	11.914(10)
b (Å)	15.5358(17)	28.807(6)	14.4292(10)	16.777(6)	17.070(5)	10.361(4)	12.545(10)
c (Å)	13.678(2)	7.3241(14)	19.1591(15)	18.310(6)	12.725(4)	12.138(5)	15.945(13)
α (°)	90	90	90	90	90	90	90.068(16)
β (°)	90	109.352(7)	97.430(4)	90	99.338(6)	107.632(8)	92.255(16)
γ (°)	120	90	90	90	90	90	101.424(16)
V (Å^3)	2859.0(6)	1957.5(6)	2007.3(3)	2257.1(14)	2391.8(12)	1941.0(14)	2334(3)
Z	6	4	4	4	4	4	4
ρ_{calc} g cm^{-1}	1.897	1.964	1.887	1.826	1.762	1.904	1.794
Temperature (K)	120	120	120	120	120	120	120
Min/Max Θ, (°)	1.51/30.02	1.41/29.96	1.77/30.06	2.51/29.39	2.25/29.59	2.69/29.99	2.48/29.69
Scan type	w-scan						
Radiation λ(Mo Kα) (Å)	0.71073						
Linear absorption (μ) (cm^{-1})	2.73	4.05	2.64	2.44	2.32	2.71	2.37
T_{min}/T_{max}	0.947/0.947	0.888/0.988	0.628/0.932	0.935/0.935	0.977/0.995	0.201/0.744	0.976/0.995
$F(000)$	1596	1128	1120	1224	1256	1088	1240
Total reflection (R_{int})	33 677(0.025)	7092(0.040)	13358(0.014)	18040(0.029)	16489(0.032)	22069(0.053)	18672(0.070)
Number of independent reflections	5511	3979	5800	6571	6816	5580	10011
Number of independent reflections with $I > 2(\sigma)$	4156	3006	4706	5122	4155	3265	6404
Parameters	328	325	354	370	380	337	757
wR_2	0.0989	0.0917	0.1168	0.1059	0.1108	0.0695	0.1542
R_1	0.0443	0.0382	0.0402	0.0509	0.0507	0.0356	0.0662
Goodness-of-fit	0.974	0.981	1.037	0.997	0.944	0.941	0.933
ρ_{max}/ρ_{min} (e Å^{-3})	0.63/−0.23	0.39/−0.26	0.58/−0.25	0.38/−0.26	0.43/−0.27	0.31/−0.26	0.62/−0.51

Table 3
The principal experimental and calculated structural parameters of studied compounds

	2a[a]	2b	2d	2f	2g	2i	2k
Experimental parameters							
Si(1)–C(1)	1.856(3)	1.875(2)	1.872(1)	1.881(3)	1.887(2)	1.844(2)	1.798(5)
Si(1)–C(11)	1.886(2)	1.882(2)	1.886(1)	1.881(3)	1.893(2)	1.886(2)	1.886(4)
Si(1)–C(21)	1.886(2)	1.886(2)	1.891(1)	1.890(3)	1.893(2)	1.883(2)	1.882(4)
Si(1)–C(31)	1.886(2)	1.880(3)	1.896(1)	1.885(3)	1.894(2)	1.897(2)	1.879(4)
C(1)–C(2)			1.499(2)	1.508(4)	1.527(3)	1.315(3)	1.216(4)
C(1)Si(1)C(11)	110.1(2)	108.0(1)	105.78(6)	103.1(1)	103.8(10)	107.82(8)	107.8(2)
C(1)Si(1)C(21)	110.1(2)	112.4(1)	112.00(6)	111.6(1)	112.1(1)	111.80(8)	112.8(2)
C(1)Si(1)C(31)	110.1(2)	105.9(1)	112.58(6)	114.4(1)	110.94(9)	110.63(8)	106.7(2)
C(11)Si(1)C(21)	109.0(2)	111.4(1)	110.29(9)	110.4(1)	111.5(1)	109.45(8)	108.9(2)
C(11)Si(1)C(31)	109.0(2)	112.8(1)	109.9(1)	111.2(1)	110.94(9)	112.85(7)	111.5(2)
C(21)Si(1)C(31)	109.0(2)	106.3(1)	106.3(1)	106.3(1)	104.44(9)	104.32(7)	108.7(2)
C(11)Si(1)C(1)C(2)		41.2(2)	62.5(1)	38.4(2)	57.5(2)	3.5(2)	71.2(2)
Calculated parameters[b]							
Si(1)–C(1)	1.852/1.854		1.874/1.874	1.889/1.874	1.890/1.891	1.844/1.846	1.799/1.798
Si(1)–C(11)	1.891/1.878		1.889/1.879	1.887/1.876	1.891/1.883	1.877/1.880	1.887/1.888
Si(1)–C(21)	1.891/1.884		1.890/1.886	1.893/1.886	1.892/1.886	1.882/1.877	1.879/1.888
Si(1)–C(31)	1.891/1.884		1.889/1.881	1.890/1.884	1.894/1.886	1.887/1.888	1.886/1.899
N(1)–C(2)			1.494/1.487	1.500/1.500	1.507/1.504	1.343/1.342	1.234/1.239
C(1)Si(1)C(11)	110.5/110.5		107.30/107.0	104.1/105.8	107.5/104.8	108.7/110.2	107.0/118.1
C(1)Si(1)C(21)	110.5/109.1		113.2/112.0	112.2/115.4	112.4/112.1	112.3/113.0	113.0/108.3
C(1)Si(1)C(31)	110.5/107.2		113.8/111.9	110.7/114.4	114.0/114.1	112.4/111.5	107.1/110.9
C(11)Si(1)C(21)	108.4/108.6		110.4/109.6	111.1/111.1	108.8/109.5	109.1/108.6	109.3/103.3
C(11)Si(1)C(31)	108.4/111.6		110.2/110.2	110.4/111.4	110.8/110.6	111.3/108.8	111.0/107.2
C(21)Si(1)C(31)	108.4/110.5		101.8/106.2	103.5/98.9	103.2/105.7	103.0/104.5	108.9/108.7
C(11)Si(1)C(1)C(2)			70.01/59.7	42.9/43.1	63.8/57.3	2.9/4.5	73.9/159.9
Binding energy	17.6		15.36	21.38	22.02	16.91	20.13

[a] The averaged values of three independent molecules are shown.
[b] The bond lengths and bond angles for molecules in crystal and isolated state are separated by "/" character.

distortion of the angle between the plane of pentafluorophenyl ring C(11)···C(16) and silicon–carbon bond Si(1)–C(11) may be clearly seen from Fig. 8 and amounts to 11.2°, while the same angles at the rest of C_6F_5 groups do not exceed 3–4°. Taken together the noticed features allow one to suggest the realization of
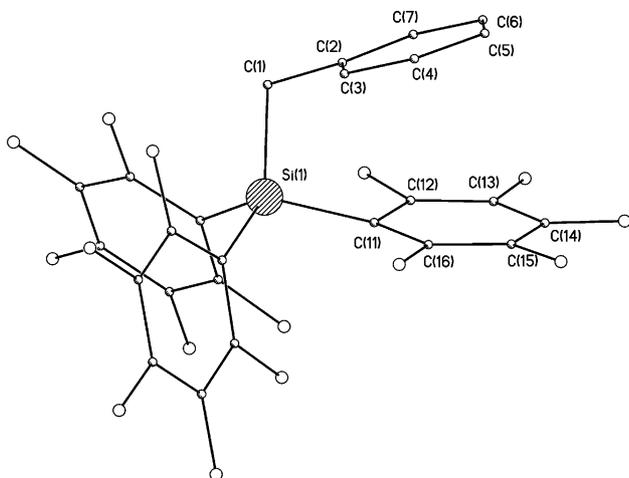

Fig. 8. The distortion of C(11) atom valence environment in **2f**.

pi···pi intramolecular interaction in the structure of **2f**. The proposed intramolecular C–H···pi and pi···pi interactions in **2i** and **2f** may be caused by steric restraints or forces of crystalline packing and may not be favored in isolated molecules.

In order to understand the role of crystalline packing in stabilization of observed molecular structures we carried out the quantum chemistry calculations using periodic boundary conditions at DFT level. For consistency only molecules with the same type of atoms, **2a**, **d**, **f**, **g**, **i**, **k**, were considered, while calculations of **2b** (R = CH_2Cl) were not performed. To mimic the isolated molecule all but one molecule were removed from the crystal cell and to avoid interactions between periodic images the parameters of the crystal cell were increased (see computational details). By using the same level of theory for calculation, the comparison of total energies of crystal and isolated molecules gave us the binding energy, which is useful for estimation of influence of crystalline packing on geometry of molecules.

The optimization of atomic positions reproduced the bond lengths and angles with sufficient accuracy. The main differences (up to 0.03 Å) from experimental values are observed in the case of C–F bonds and for C(1)–C(2) bond in vinyl group of compound **2i**. The

Si–C and C–C bond lengths were reproduced within 0.015 Å. In general, both in crystal and in isolated molecules the relative positions of substituent R and C_6F_5 rings predicted by quantum chemistry calculations are close to those in experiment. The considerable differences between crystal and isolated molecules are observed in the case of compounds where the presence of pi···pi intramolecular interaction were proposed (vide supra). In isolated molecule of **2f** the interplanar angle and C···C interatomic distances are changed to 47° and 3.63 Å, respectively, as compared to crystal. Also, the angle between plane of C(11)···C(16) pentafluorophenyl ring and Si(1)–C(11) bond is decreased to 3.4° in comparison with calculated values in crystal (12.8°). So, we may conclude that the influence of crystal field led to the parallel orientation of phenyl and C_6F_5 rings and proposed pi···pi interaction between them is not favorable. On the other hand, in isolated molecule of compound **2i** the interatomic distance C(11)···H(1) is nearly the same in experimental and calculated crystal structures, a fact which can be attributed to the formation of attractive C–H···pi contact.

The presence of many fluorine atoms causes the appearance of C–H···F and F···F contacts in crystal structures of **2a**, **b**, **d**, **f**, **g**, **i**, **k** [17]. The closest F···F contacts (2.65 Å) in experimental crystal structure were observed in **2a** (R = Me), as well as the strongest C–H···F contact (2.37 Å) occurred in **2f** (R = CH$_2$Ph). The optimization of atomic positions in general led to some shortening of F···F and H···F interatomic distances by approximately 0.1 Å (Table 3). Such errors in definition of weak intermolecular contacts are typical for modern DFT functionals which cannot account for nonlocal dispersion interactions. At the same time the calculations reproduced well the intermolecular stacking interaction in **2g** (Fig. 9), where the phenyl ring is projected onto C_6F_5-group. The calculated and experimental interatomic distances between centroid of former ring and C(14) atom of the latter one constitute 3.40 and 3.41 Å, respectively, while interplanar angles in both cases are equal to 7.1°. The stacking interaction of similar type was found in perfluorinated tolanes [18]. The values of interplanar angles and interplanar separation were in the range of 5–9° and 3.4–3.5 Å, correspondingly.

Despite shortening of F···F and H···F interatomic distances the total number of intermolecular contacts changes insignificantly, so one may believe that calculated binding energies should be reliable for characterization of studied structures. Also it should be noted that the presence of short interatomic distances between pair of atoms is not a sufficient criterion for attractive interaction [19]. In order to study the nature and strength of F···F and H···F contacts, we plan in future to investigate the electron density distribution function in terms of Bader's "Atoms in molecules" theory [20].

The calculated binding energies (Table 3) correspond to sublimation energies at 0 K and therefore may correlate with the magnitude of crystal melting (Table 2). Analysis of these values did not reveal the exact correlation, presumably because melting point is defined not only by enthalpy of sublimation. Nevertheless, one may see that the lowest value of binding energy is found for compound **2d** (R = allyl) which is characterized by low melting point. Anomalously low melting point of **2d** may also be explained by the presence of flexible allyl group that is in agreement with corresponding values for **2e** (R = 2-methallyl) and **2j** (R = trans-PhCH=CH) – they also have flexible groups and rather low melting points.

Without studies of electron density it is difficult to completely investigate the influence of intermolecular interactions on the structure and physical properties of compounds of such class. On qualitative level one may explain the observed tendency by different number of F···F and C–H···F contacts in crystal packing of investigated compounds. In the case of methyl (**2a**) and vinyl (**2i**) derivatives the number of C–H···F intermolecular contacts is significantly lower than that in compounds with more bulky R groups. Probably, an increase of number of hydrogen atoms in R group leads to corresponding increase of number of C–H···F contacts, which are stronger than F···F ones. On the other hand the enlargement of R causes crystalline packing to be more "loose". This is in agreement with density values, the largest value corresponds to R = Me (**2a**) and vinyl (**2i**), while the least one to R = α-phenylethyl (**2g**).

From experimental and theoretical structural studies the following generalizations may be formulated: the TPFS group possesses considerable steric bulk, which is further augmented by the tendency to shorten the carbon–silicon bond C–Si(C_6F_5)$_3$, and that the structure of
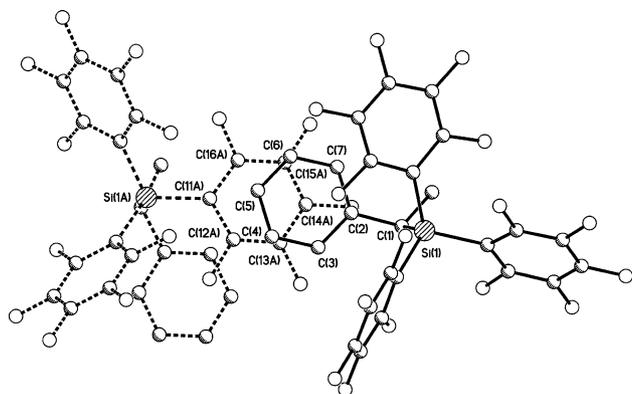

Fig. 9. Stacking interaction in crystal structure of **2g**. The molecule A is drawn with dashed lines obtained by following symmetry operations: −0.5 + x, 0.5 −y, −0.5 + z.

TPFS unit in the solid state may be affected by the fourth substituent and by forces of crystalline packing.

3. Conclusion

Herein we presented a convenient procedure for the synthesis of TPFS derivatives. The ready availability of this compounds opens up opportunity for investigation of their synthetic applications. Given the significant steric requirements of the TPFS group, the diminished reactivity of the adjacent carbon atoms may be expected. At the same time, the presence of three electron withdrawing pentafluorophenyl rings can make the silicon atom susceptible to nucleophilic activation. Studies along these lines are in progress in our laboratories.

4. Experimental

Bromopentafluorobenzene was purchased from P&M Invest and was used as received. Silanes **1b** [21], **1d,e** [22], **1f** [23], **1g** [24], **1j** [25], **1k** [26] were synthesized according to literature procedures; others were commercial products (Aldrich, Acros).

Bromopentafluorobenzene (3.25 mL, 26.0 mmol) was added dropwise to a suspension of magnesium turnings (0.625 g, 26.0 mmol) in diethyl ether (14 ml) at such a rate to maintain gentle reflux. After complete addition the mixture was refluxed for additional 1 h and cooled with ice/water bath. Trichlorosilane **1** (8.4 mmol) and THF (14 mL) were successively added dropwise. The cooling bath was removed and the mixture was refluxed for 1 h. After cooling to room temperature, the mixture was diluted with hexane (14 mL, for **2a–f, h, i**) or with toluene (14 mL, for **2g, j, k**), and filtered. The filter cake was washed with hexane (for **2a–f, h, i**) or with toluene (for **2g, j, k**). The combined filtrate was washed with water (2 × 20 mL), dried (MgSO₄) and concentrated under vacuum to give crude product which was distilled in vacuum.

Distillation of **2c–f, k** afforded pure substances, while for **2a, b, g–j** the recrystallization was necessary. The yields given in Table 1 correspond to pure material.

In large scale syntheses extra care should be taken after the addition of THF, since removal of cooling bath and warming causes the spontaneous exothermic reaction accompanying by the precipitation of magnesium salts. At this point the external cooling has to be applied. After calming down the reaction the mixture was refluxed for 1 h as in standard procedure.

Methyltris(pentafluorophenyl)silane (2a). B.p. 127–135 °C/0.5 Torr. Distilled product was recrystallized from hexane. M.p. 89–90 °C. NMR ^{1}H (CDCl₃), δ: 1.17 (sept, 3H, $^5J_{C-F}$ = 1.5, CH₃); NMR ^{13}C, δ: −0.2 (sept, $^4J_{C-F}$ = 3.1, CH₃), 105.1 (t, $^2J_{C-F}$ = 27.4, C$_{i-C6F5}$), 137.6 (dm, $^1J_{C-F}$ = 254, CF), 143.6 (dm, $^1J_{C-F}$ = 258, CF), 149.3 (dm, $^1J_{C-F}$ = 245, CF). NMR ^{19}F, δ: −160.1 (m, *meta*), −147.7 (tt, J_{F-F} = 4.4, 19.8, *para*), −127.2 (d, J_{F-F} = 17.0, *ortho*). IR (KBr, cm^{-1}) 1645 (w), 1523 (m), 1469 (st), 1380 (w), 1292 (w), 1093 (m), 972 (m), 807 (w), 514 (w), 422 (w). Anal. Calc. for C₁₉H₃F₁₅Si: C, 41.93; H, 0.56. Found: C, 42.01; H, 0.42%.

Chloromethyltris(pentafluorophenyl)silane (2b). B.p. 130–134 °C/0.2 Torr. Distilled product was recrystallized from hexane. M.p. 119–122 °C (hexane). NMR ^{1}H (CDCl₃), δ: 3.69 (s, 2H, CH₂); NMR ^{13}C, δ: 26.9 (sept, $^4J_{C-F}$ = 3.4, CH₂), 102.5 (t, $^2J_{C-F}$ = 29.5, C$_{i-C6F5}$), 137.6 (dm, $^1J_{C-F}$ = 254, CF), 144.0 (dm, $^1J_{C-F}$ = 260, CF), 149.4 (dm, $^1J_{C-F}$ = 247, CF). NMR ^{19}F, δ: −159.5 (m, *meta*), −146.3 (tt, J_{F-F} = 4.4, 20.1, *para*), −126.2 (d, J_{F-F} = 18.4, *ortho*). IR (KBr, cm^{-1}) 1646 (w), 1521 (m), 1476 (st), 1383 (w), 1292 (w), 1102 (m), 1089 (m), 973 (m). Anal. Calc. for C₁₉H₂ClF₁₅Si: C, 39.43; H, 0.35. Found: C, 39.33; H, 0.43%.

(3-Chloropropyl-1)tris(pentafluorophenyl)silane (2c). B.p. 140–154 °C/0.4 Torr. M.p. 106–111 °C (hexane). NMR ^{1}H (CDCl₃), δ: 1.78–1.88 (m, 4H, CH₂CH₂Si), 3.58 (t, 2H, J = 6.0, CH₂Cl), NMR ^{13}C, δ: 12.8 (br, CH₂–Si), 26.6 (*CH₂*CH₂Si), 46.5 (CH₂Cl), 104.0 (t, $^2J_{C-F}$ = 28.2, C$_{i-C6F5}$), 137.6 (dm, $^1J_{C-F}$ = 255, CF), 143.7 (dm, $^1J_{C-F}$ = 258, CF), 149.3 (dm, $^1J_{C-F}$ = 246, CF). NMR ^{19}F, δ: −160.0 (m, *meta*), −147.5 (tt, J_{F-F} = 4.1, 19.8, *para*), −126.8 (d, J_{F-F} = 17.7, *ortho*). IR (KBr, cm^{-1}) 1645 (m), 1520 (st), 1474 (st), 1384 (w), 1293 (w), 1090 (st), 973 (st), 702 (w), 514 (w), 422 (w). Anal. Calc. for C₂₁H₆ClF₁₅Si: C, 41.57; H, 1.00. Found: C, 41.34, 1.30%.

3-Propenyltris(pentafluorophenyl)silane (2d). B.p. 124–127 °C/0.25 Torr. M.p. 48–51 °C. NMR ^{1}H (CDCl₃), δ: 2.64 (d, 2H, J = 7.8, CH₂Si), 4.93–4.99 (m, 2H, C*H₂* = CH), 5.69–5.80 (m, 1H, CH); NMR ^{13}C (CDCl₃), δ: 22.2 (br., CH₂Si), 104.1 (t, $^2J_{C-F}$ = 29.8, C$_{i-C6F5}$), 118.1 (CH), 129.6 (CH₂=), 137.6 (dm, $^1J_{C-F}$ =255, CF), 143.7 (dm, $^1J_{C-F}$ = 259, CF), 149.2 (dm, $^1J_{C-F}$ = 245, CF); NMR ^{19}F (CDCl₃), δ: −160.7 (m, *meta*), −148.2 (tt, J = 4.5, 20.3, *para*), −127.0 (d, J = 18.1, *ortho*). IR (KBr, cm^{-1}) 1644 (w), 1521 (m), 1469 (st), 1381 (w), 1294 (w), 1091 (st), 975 (st) 787 (w), 518 (w), 435 (w). Anal. Calc. for C₂₁H₅F₁₅Si: C, 44.22; H, 0.88. Found: C, 44.01, 0.88%.

(2-Methylpropenyl-3)tris(pentafluorophenyl)silane (2e). B.p. 135–145 °C/0.27 Torr. M.p. 74–78 °C. NMR ^{1}H (CDCl₃), δ: 1.69 (s, 3H, CH₃), 2.76 (s, 2H, CH₂–Si), 4.50 (s, 1H), 4.66 (s, 1H) (=CH₂). NMR ^{13}C, δ: 24.0 (CH₂Si), 104.8 (t, $^2J_{C-F}$ = 28.7, C$_{i-C6F5}$), 113.0 (CH₂=), 137.7 (dm, $^1J_{C-F}$ = 255, CF), 137.7 (C=CH₂), 143.7 (dm, $^1J_{C-F}$ = 258, CF), 149.5 (dm, $^1J_{C-F}$ = 245, CF). NMR ^{19}F, δ: −160.7 (m, *meta*), −148.4 (br,

para), −126.1 (d, J_{F-F} = 18.0, ortho). IR (KBr, cm^{-1}) 1645 (w), 1519 (m), 1471 (st), 1381 (w), 1290 (w), 1090 (m), 970 (m), 531 (w), 432 (w). Anal. Calc. for $C_{22}H_7F_{15}Si$: C, 45.22; H, 1.21. Found C, 45.27; H, 1.23%.

Benzyltris(pentafluorophenyl)silane (2f). B.p. 133–141 °C/0.07 Torr. M.p. 132–134 °C (hexane). NMR ^{1}H (CDCl$_3$), δ: 3.27 (s, 3H, CH$_2$–Si), 6.90–6.93 (m, 2H, Ph), 7.08–7.15(m, 3H, Ph); NMR ^{13}C, δ: 23.9 (sept., $^4J_{C-F}$ = 2.5, CH$_2$–Si), 104.3 (t, $^2J_{C-F}$ = 29.6, C$_{i-C6F5}$), 126.2, 128.2, 128.7 (CH$_{Ph}$), 134.6 (C$_{i-Ph}$), 137.5 (dm, $^1J_{C-F}$ = 255, CF), 143.5 (dm, $^1J_{C-F}$ = 259, CF), 149.0 (dm, $^1J_{C-F}$ = 246, CF). NMR ^{19}F, δ: −160.0 (m, *meta*), −147.5 (tt, J_{F-F} = 4.1, 20.0, *para*), −125.6 (d, J_{F-F} = 17.7, *ortho*). IR (KBr, cm^{-1}) 1644 (w), 1519 (m), 1475 (st), 1379 (w), 1293 (w), 1093 (m), 972 (m), 741 (w), 521 (w). Anal. Calc. for $C_{25}H_7F_{15}Si$: C, 48.40; H, 1.14. Found: C, 48.13, 1.31%.

(1-Phenylethyl-1)tris(pentafluorophenyl)silane (2g). Sublimation 160–164 °C (bath temperature)/0.4 Torr. Sublimed product was recrystallized from dichloroethane. M.p. 182–188 °C. NMR ^{1}H (CDCl$_3$), δ: 1.56 (d, 3H, J = 7.6, Me), 3.89 (q, 1H, J = 7.6, CHSi), 6.92–6.96 (m, 2H, Ph), 7.12–7.19 (m, 3H, Ph); NMR ^{13}C, δ: 14.3 (Me), 26.9 (CHSi), 104.2 (t, $^2J_{C-F}$ = 30.0, C$_{i-C6F5}$), 126.6, 127.0, 128.6 (CH$_{Ph}$), 139.6 (C$_{i-Ph}$), 137.5 (dm, $^1J_{C-F}$ = 255, CF), 143.4 (dm, $^1J_{C-F}$ = 259, CF), 148.9 (dm, $^1J_{C-F}$ = 246, CF). NMR ^{19}F, δ: −160.0 (m, *meta*), −147.8 (t, J_{F-F} = 19.8, *para*), −124.4 (d, J_{F-F} = 18.4, *ortho*). IR (KBr, cm^{-1}) 1644 (m), 1520 (m), 1477 (st) 1470 (st), 1378 (w), 1293 (m), 1089 (st), 975 (m), 521 (w). Anal. Calc. for $C_{26}H_9F_{15}Si$: C, 49.22; H, 1.43. Found: C, 49.12, 1.57%.

Phenyltris(pentafluorophenyl)silane (2h). B.p. 185–187 °C/0.5 Torr. Distilled product was recrystallized from hexane. M.p. 135–136 °C [9a].

Vinyltris(pentafluorophenyl)silane (2i). B.p. 140–150 °C (bath temperature)/0.2 Torr. Distilled product was recrystallized from hexane. M.p. 117–119 °C. NMR ^{1}H (CDCl$_3$), δ: 5.84 (d, 1H, J = 19.7), 6.39 (dd, 1H, J = 2.3, 14.4), 6.73 (ddm, 1H, J = 14.4, 19.7); NMR ^{13}C δ: 127.9, 138.8 (CH$_2$=CH), 103.9 (t, $^2J_{C-F}$ = 29.8, C$_{i-C6F5}$), 137.6 (dm, $^1J_{C-F}$ = 253, CF), 143.8 (dm, $^1J_{C-F}$ = 257, CF), 149.3 (dm, $^1J_{C-F}$ = 244, CF). NMR ^{19}F, δ: −161.2 (m, *meta*), −148.6 (tt, J_{F-F} = 4.4, 19.5, *para*), −126.9 (d, J_{F-F} = 18.2, *ortho*). IR (KBr, cm^{-1}) 1644 (m), 1520 (st), 1478 (st), 1469 (st), 1382 (m), 1294 (m), 1087 (st), 975 (st), 702 (w), 557 (w), 527 (w), 454 (w). Anal. Calc. for $C_{21}H_3F_{15}Si$: C, 43.18; H, 0.54. Found: C, 43.24, 0.60%.

Trans-Phenylethenyltris(pentafluorophenyl)silane (2j). B.p. 169–174 °C/0.4 Torr. Distilled product was treated with hexane/i-PrOH mixture to cause crystallization. M.p. 72–75 °C. NMR ^{1}H (CDCl$_3$), δ: 6.92 (d, 1H, J = 18.9), 7.01 (d, 1H, J = 18.9) (CH=CH), 7.36–7.42 (m, 3H, Ph), 7.49–7.52 (m, 2H, Ph). NMR ^{13}C, δ:

104.3 (t, $^2J_{C-F}$ = 27.3, C$_{i-C6F5}$), 115.7 (CH−Si), 127.3, 128.8, 129.9 (3 CH$_{Ph}$), 136.6 (C$_{i-Ph}$), 137.6 (dm, $^1J_{C-F}$ = 255, CF), 143.7 (dm, $^1J_{C-F}$ = 259, CF), 149.3 (dm, $^1J_{C-F}$ = 246, CF), 151.1 (CH=CHSi). NMR ^{19}F, δ: −159.9 (m, *meta*), −147.4 (tt, J_{F-F} = 4.1, 19.8, *para*), −126.0 (d, J_{F-F} = 18.4, *ortho*). IR (KBr, cm^{-1}) 1645 (w), 1519 (w), 1470 (st), 1382 (w), 1092 (m), 973 (m). Anal. Calc. for $C_{26}H_7F_{15}Si$: C, 49.38; H, 1.12. Found: C, 49.40, 1.35%.

Phenylethynyltris(pentafluorophenyl)silane (2k). B.p. 170–175 °C (bath temperature)/0.1 Torr. M.p. 130–133 °C (hexane). ^{1}H NMR (CDCl$_3$), δ: 7.39 (t, 2H, ^3J = 7.5), 7.45 (t, 1H, ^3J = 7.5), 7.59 (d, 2H, ^3J = 7.5). NMR ^{13}C, δ: 81.9 (C≡C), 103.7 (t, $^2J_{C-F}$ = 26.3, C$_{i-C6F5}$), 111.6 (C≡C), 121.1 (C$_{i-Ph}$), 128.5, 130.3, 132.5 (3 CH$_{Ph}$), 137.7 (dm, $^1J_{C-F}$ = 254, CF), 144.0 (dm, $^1J_{C-F}$ = 259, CF), 149.5 (dm, $^1J_{C-F}$ = 246, CF). NMR ^{19}F, δ: −160.1 (m, *meta*), −147.1 (tt, J_{F-F} = 4.4, 19.8, *para*), −126.5 (d, J_{F-F} = 17.7, *ortho*). IR (KBr, cm^{-1}) 2174 (m), 1645 (m), 1518 (st), 1478 (st), 1382 (m), 1294 (m), 1095 (st), 973 (st), 763 (w), 521 (w) 438 (w). Anal. Calc. for $C_{26}H_5F_{15}Si$: C, 49.54; H, 0.80. Found: C, 49.40; H, 0.79%.

Computational details.

The quantum chemistry calculations were carried out using CPMD 3.7.2 [27] density functional (DFT) code. For the optimizations of atomic position (started from experimental crystal structures) in crystal simulated annealing technique was used followed by BFGS minimization of total energy. Vanderbilt's ultrasoft pseupotentials [28] have been applied to account of core electrons while valence electrons were approximated by plane-wave expansion with 25 Ry cutoff. Exchange and correlation terms of total energy were described by LDA approximation. Kohn-Sham equations were integrated using Γ-point approximation. We believe that such approximation is sufficient because of rather large crystal cells. DFT does not take into account dispersion interactions, so calculated cell parameters may be systematically overestimated or underestimated up to 5%. Thus, the experimental values of cell parameters were used in calculations. Atomic displacements converged better than 10^{-4} a.u., as well as energy variations were less than 10^{-6} a.u.

The isolated molecules were simulated utilizing the same theoretical background, basis sets and convergence criteria by quantum chemistry calculation of single molecule in cubic box with side 15 Å. The structures of isolated molecules were tested on stability by calculation of vibrational frequencies.

5. Supplementary materials

Crystallographic data are deposited with the Cambridge Crystallographic Data Centre and are available free of charge at CCDC, 12 Union Road, Cambridge

CB2 1EZ, UK, fax: +44 0 1223 336 033, e-mail: deposit @ccdc.cam.ca.uk. CCDC ref codes: 262523 (**2a**), 262524 (**2b**), 262525 (**2d**), 262526 (**2f**), 262527 (**2g**), 262528 (**2i**), 262529 (**2k**).

References

[1] (a) M. Nakash, M. Goldvaser, J. Am. Chem. Soc. 126 (2004) 3436;
(b) R.J.P. Corriu, M. Granier, G.F. Lanneau, J. Organomet. Chem. 562 (1998) 79;
(c) R. Pietschnig, F. Belaj, J. Tirree, J. Organomet. 23 (2004) 4897.

[2] B. Boury, R.J.P. Corriu, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 3, Wiley, Chichester, UK, 2001, pp. 565–640.

[3] (a) S. Kobayashi, M. Sugiura, C. Ogawa, Adv. Synth. Catal. 346 (2004) 1023;
(b) S.E. Denmark, R.A. Stavenger, Acc. Chem. Res. 33 (2000) 432;
(c) H. Sakurai, Synlett (1989) 1;
(d) S. Kobayashi, K. Nishio, J. Org. Chem. 59 (1994) 6620;
(e) A.V. Malkov, L. Dufkova, L. Farrugia, P. Kocovsky, Angew. Chem., Int. Ed. Engl. 42 (2003) 3674;
(f) K. Kubota, J.L. Leighton, Angew. Chem., Int. Ed. Engl. 42 (2003) 946.

[4] (a) C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, Chem. Rev. 93 (1993) 1371;
(b) D. Kost, I. Kalikhman, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, UK, 1998, p. 1339.

[5] A.J. Blake, S. Cradock, E.A.V. Ebsworth, K.C. Franklin, Angew. Chem., Int. Ed. Engl. 29 (1990) 76.

[6] A.R. Bassindale, S.J. Glynn, P.G. Taylor, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, UK, 1998, pp. 495–511.

[7] (a) Pentafluorophenylboron derivatives: K. Ishihara, H. Yamamoto, Eur. J. Org. Chem. (1999) 527;
(b) J.M. Blackwell, W.E. Piers, R. McDonald, J. Am. Chem. Soc. 124 (2002) 1295;
(c) T. Schwier, M. Rubin, V. Gevorgyan, Org. Lett. 6 (2004) 1999;
(d) Pentafluorophenylphosphorous derivatives:A.L. Fernandez, M.R. Wilson, A. Prock, W.P. Giering, Organometallics 20 (2001) 3429;
(e) H.J.V. Barros, M.L. Ospina, E. Arguello, W.R. Rocha, E.V. Gusevskaya, E.N. dos Santos, J. Organomet. Chem. 671 (2003) 150;
(f) For examples of pentafluorophenyl derivatives of Ge, Sn, Pb, Ti, and Zr, see:C. Tamborski, E.J. Sloloski, S.M. Dec, J. Organomet. Chem. 4 (1965) 446.

[8] (a) L.A. Wall, R.E. Donadio, W.J. Pummer, J. Am. Chem. Soc. 82 (1960) 4846;
(b) P.L Coe, R. Stephens, J.C. Tatlow, J. Chem. Soc. (1962) 3227;

(c) E.J. Harper Jr., E.J. Soloski, C. Tamborski, J. Org. Chem. 29 (1964) 2385.

[9] (a) PhSi(C$_6$F$_5$)$_3$, H.-J. Frohn, A. Lewin, V.V. Bardin, J. Organomet. Chem. 568 (1998) 233;
(b) PhCH = CHSi(C$_6$F$_5$)$_3$ and CH$_2$ = C(Ph)Si(C$_6$F$_5$)$_3$ T. Brennan, H. Gilman, J. Organomet. Chem. 16 (1969) 63;
(c) Si(C$_6$F$_5$)$_4$, see ref 8a.

[10] Reaction of *ortho*-tolyltrichlorosilane with excess of *ortho*-methoxyphenylmagnesium bromide affords product of substitution of only two chlorines, see: I.I. Lapkin, F.G. Mukhina, N.F. Kirilov, L.P. Sheshina, M.S. Kozhevnikova, Zh. Obsch. Khim. 54 (1984) 2039 (Russ. J. Org. Chem. 54 (1984) 1820).

[11] (a) The acceleration of nucleophilic attack at the silicon atom with the introduction of pentafluorophenyl group was documented: A.L. Klebanskii, Yu.A. Yuzhelevskii, E.G. Kagan, G.A. Nikolaev, A.V. Harlamova, Zh. Obsch. Khim. 38 (1968) 914 (Russ. J. Gen. Chem. 38 (1968) 878);
(b) For pertinent discussion on reaction of pentafluorophenylmagnesium bromide with tetraethoxysilane see: A. Whittingham, A.W.P. Jarvie, J. Organomet. Chem. 13 (1968) 125.

[12] The yield of 80% for the synthesis of **2h** from PhSiCl$_3$ and C$_6$F$_5$Li was reported: M. Schmeisser, N. Wessal, M. Weidenbruch, Chem. Ber. 101 (1968) 1897, However, in this reaction we could not achieve the yield greater than 60%.

[13] (a) A.D. Dilman, P.A. Belyakov, A.A. Korlyukov, V.A. Tartakovsky, Tetrahedron Lett. 45 (2004) 3741;
(b) V.V. Levin, A.D. Dilman, P.A. Belyakov, A.A. Korlyukov, M.I. Struchkova, V.A. Tartakovsky, Eur. J. Org. Chem. (2004) 5141.

[14] CCDC ref code PFPSIL: A. Karipides, B. Foerst, Acta Crystallogr., Sect. B 34 (1978) 3494.

[15] To avoid systematic errors in single crystal X-ray analysis C–H bonds were normalized to 1.08 Å obtained from single crystal neutron studies, see: F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1987) S1.

[16] Search in Cambridge data base revealed 35 ordered structures of vinyl silanes with terminal CH$_2$ group, from which only one compound has shorter C$\cdots$H contact of 2.64 Å; CH$_2$=C(Ph)SiPh$_3$, ref code VOLZAX, L.N. Lewis, K.G. Sy, G.L. Bryant, P.E. Donahue, Organometallics 10 (1991) 3750.

[17] According to Rowland and Taylor F$\cdots$F and H$\cdots$F intermolecular contacts should be as much as 2.90 and 2.54 Å, respectively. R.S. Rowland, R. Taylor, Phys. Chem. 100 (1996) 7384.

[18] C.E. Smith, P.S. Smith, R.Ll. Thomas, E.G. Robins, J.C. Collings, C. Dai, A.J. Scott, S. Borwick, A.S. Batsanov, S.W. Watt, S.J. Clark, C. Viney, J.A.K. Howard, W. Clegg, T.B. Marder, J. Mater. Chem. 14 (2004) 413.

[19] (a) Several papers describe such examples: A.A. Korlyukov, K.A. Lyssenko, M.Yu. Antipin, A.G. Shipov, O.A. Zamyshlyaeva, E.P. Kramarova, Vad.V. Negrebetsky, S.A. Pogozhikh, Yu.E. Ovchinnikov, Yu.I. Baukov, Russ. Chem. Bull. 9 (2004) 1846;
(b) N.R. Mitzel, U. Losehand, A. Wu, D. Cremer, D.W.H. Rankin, J. Am. Chem. Soc. 122 (2000) 4471;
(c) K.A. Lyssenko, M.Yu. Antipin, D.Yu. Antonov, Chem. Phys. Chem. 4 (2003) 817.

[20] R.F.W. Bader, Atoms in Molecules. A Quantum Theory, Clarendron Press, Oxford, 1990.

[21] C.-T. Huang, P.-J. Wang, Acta Chim. Sinica 22 (1956) 123 (Chem. Abstr. 52 (1958) 5285b).

[22] N. Furuya, T. Sukawa, J. Organomet. Chem. 96 (1975) C1.

[23] R.A. Benkeser, J.M. Gaul, W.E. Smith, J. Am. Chem. Soc. 91 (1969) 3666.

[24] Y. Uozumi, H. Tsuji, T. Hayashi, J. Org. Chem. 63 (1998) 6137.

[25] V.F. Mironov, V.V. Nepomnina, Izv. Akad. Nauk SSSR Otd. Khim Nauk (1960) 1419 (Bull. Acad. Sci. USSR Div. Chem. Sci. (1960) 1318).

[26] A.D. Petrov, L.L. Schukovskaya, Zh. Obsh. Khim. 25 (1955) 1128 (Russ. J. Gen. Chem. 25 (1955) 1083).

[27] J. Hutter, P. Ballone, M. Bernasconi, P. Focher, E. Fois, S. Goedecker, M. Parrinello, Tuckerman (1995–2004) CPMD v. 3.7.2, MPI für Festkörperforschung and IBM Zurich Research Laboratory.

[28] D. Vanderbilt, Phys. Rev. B 41 (1985) 7892.