ChemPubSoc Europe
DOI: 10.1002/chem.201603442
CHEMISTRY
A European Journal
Full Paper

Silicon Chemistry

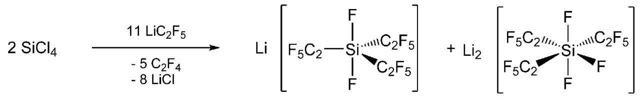
Synthesis of Functional Bis(pentafluoroethyl)silanes $(C_2F_5)_2SiX_2$, with X = H, F, Cl, Br, OPh, and O_2CCF_3

Nico Schwarze,[a] Boris Kurscheid,[a] Simon Steinhauer,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] Nikolai Ignat'ev,[b] and Berthold Hoge*[a]

Abstract: As recently shown, the introduction of pentafluoroethyl functionalities into silicon compounds is of general interest due to an enhanced Lewis acidity of the resulting species. By this means, the synthesis of previously inaccessible hypervalent silicon derivatives is enabled.[1] While an easy access to tris(pentafluoroethyl)silanes has already been published, synthetic strategies for the selective preparation of bis derivatives are yet unknown. In this contribution, a convenient protocol for the synthesis of functional bis(pentafluoroethyl)silicon compounds is presented. These compounds represent precursors for the synthesis of pentafluoroethylated polysiloxanes.[2] Furthermore, they prove to be resistant to oxonium cations, which is a key feature for the preparation of stable pentafluoroethylsilic acids.[3] Treatment of dichlorodiphenoxysilane with in situ generated pentafluoroethyl lithium leads to the corresponding bis(pentafluoroethyl)silane in high yields. $(C_2F_5)_2Si(OPh)_2$ serves as a starting material for further functionalized bis(pentafluoroethyl)silanes. These silanes have been isolated and their reactivity towards N bases studied. The pronounced Lewis acidity of the obtained compounds has been documented by the formation of octahedral adducts with nitrogen donors such as 1,10-phenanthroline and acetonitrile.

Introduction

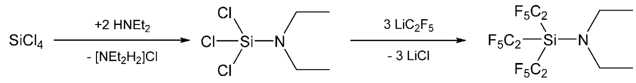
In general, pentafluoroethyl element compounds exhibit higher thermal stabilities than the trifluoromethyl analogues.[4] While $(C_2F_5)_3SiNEt_2$ shows no decomposition after 2 h at 180 °C, $(CF_3)_3SiNEt_2$ tends to violent decomposition even at room temperature.[5] A similar trend can be observed for the corresponding lithium perfluoroalkyl compounds. While $LiCF_3$ is still elusive, the persistence of LiC_2F_5 at lower temperatures renders it very useful for synthetic applications.[6] At temperatures above $-40\,^{\circ}C$, the compound decomposes under formation of C_2F_4 and LiF. The thermal stability of LiC_2F_5 strongly depends on the reaction conditions. In the presence of strong Lewis acids it decomposes even at temperatures below $-70\,^{\circ}C$. Therefore, in the presence of strong Lewis acids, LiC_2F_5 behaves as a fluoride-ion donor rather than as a C_2F_5 group transfer reagent. Both pathways are followed in the reaction of $SiCl_4$ with an excess of LiC_2F_5, giving rise to the formation of fluoro(pentafluoroethyl)silicates $[Si(C_2F_5)_3F_3]^{2-}$ and $[Si(C_2F_5)_3F_2]^{-}$ (Scheme 1).[7]



Scheme 1. Synthesis of difluoro- and trifluorotris(pentafluoroethyl)silicate by pentafluoroethylation of $SiCl_4$.

Silicate formation proceeds much faster than the C_2F_5 group transfer. Thus the reaction of $SiCl_4$ with less than four equivalents of LiC_2F_5 results in the exclusive formation of silicates, rather than in the formation of neutral tris- or bis(pentafluoroethyl)silanes.[8] In order to synthesize neutral tris(pentafluoroethyl)silanes the silicate formation has to be avoided. Attaching electron-donating groups to the silicon moiety leads to a significantly reduced Lewis acidity and allows, therefore, the selective synthesis of tris(pentafluoroethyl)silanes, such as $(C_2F_5)_3SiNEt_2$ and $(C_2F_5)_3SiCH_3$.[8]

Surprisingly, the NEt_2 group fails in the selective synthesis of bis(pentafluoroethyl)silanes (Scheme 2). It can be assumed that due to steric issues, the reaction of $Cl_2Si(NEt_2)_2$ with LiC_2F_5 gave a complex mixture with $(C_2F_5)_2SiF(NEt_2)$ as the major component. It is obvious that the selective synthesis of bis(pentafluoroethyl)silane derivatives requires less bulky electron-donating



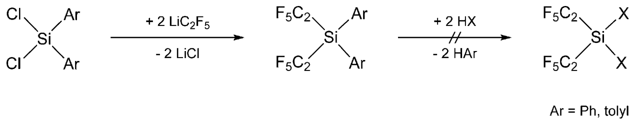
Scheme 2. Two-step synthesis of diethylaminotris(pentafluoroethyl)silane.

---

[a] N. Schwarze, Dr. B. Kurscheid, Dr. S. Steinhauer, B. Neumann,
Dr. H.-G. Stammler, Prof. Dr. B. Hoge
Centrum für Molekulare Materialien
Fakultät für Chemie, Anorganische Chemie II
Universität Bielefeld
Universitätsstrasse 25, 33615 Bielefeld (Germany)
E-mail: b.hoge@uni-bielefeld.de

[b] Dr. N. Ignat'ev
Consultant, Merck KGaA
Frankfurter Straße 250, 64293 Darmstadt (Germany)

substituents. The pentafluoroethylation of Ph_2SiCl_2 or (*p*-tolyl)$_2SiCl_2$ furnished $(C_2F_5)_2SiPh_2$ and $(C_2F_5)_2Si$(*p*-tolyl)$_2$, respectively. Because the attempted replacement of the aryl groups by halides according to Scheme 3 failed to give functionalized bis(perfluoroethyl)silanes $(C_2F_5)_2SiX_2$ we envisaged the phenoxy functionality as a leaving group.



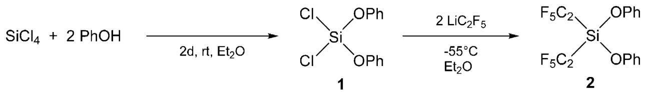
Scheme 3. Attempts to prepare functional bis(pentafluoroethyl)silanes by introduction of aryl groups.

In this article we report on the successful employment of phenoxy groups for the high-yield synthesis of $(C_2F_5)_2Si(OPh)_2$ in multigram quantities. Further derivatization of $(C_2F_5)_2Si(OPh)_2$ constitutes a route to a whole library of bis(pentafluoroethyl)silanes, $(C_2F_5)_2SiX_2$, with X = H, F, Cl, Br, and CF_3CO_2. The pronounced Lewis acidity of the obtained compounds is documented by the formation of octahedral adducts with nitrogen donors, such as 1,10-phenanthroline and acetonitrile, $[Si(C_2F_5)_2X_2(phen)]$ and $[Si(C_2F_5)_2X_2(NCCH_3)_2]$, respectively.

Results and Discussion

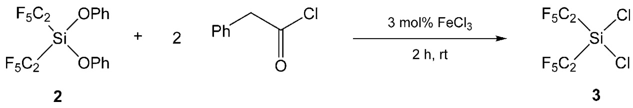
Synthesis of bis(pentafluoroethyl)silanes

Dichlorodiphenoxysilane (**1**) was envisaged as an appropriate starting material for the selective synthesis of bis(pentafluoroethyl)silane derivatives. Stirring phenol with silicon tetrachloride in diethyl ether at room temperature for two days afforded compound **1** in a 73% yield on a 100 g scale.[9] Subsequent treatment of **1** with in situ generated pentafluoroethyllithium in diethylether at −85 °C yields bis(pentafluoroethyl)diphenoxysilane (**2**) as a colorless liquid in 74% yield (Scheme 4). Diphenoxysilane **2** represents a colorless liquid that can be handled with common Schlenk techniques.



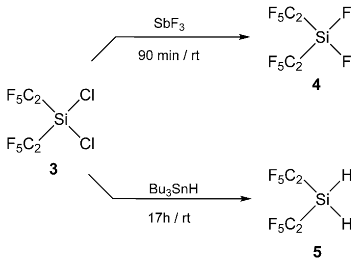
Scheme 4. Synthesis of dichlorodiphenoxysilane (**1**) and the subsequent reaction with pentafluoroethyllithium yielding bis(pentafluoroethyl)diphenoxysilane (**2**).

Combining **2** with an excess of phenylacetyl chloride for six days at 65 °C leads to the corresponding dichlorosilane **3** in 88% yield (Scheme 5).[10a] Addition of catalytic amounts of iron trichloride accelerates the reaction significantly.[10b] Product **3** was obtained as a colorless liquid with a vapor pressure of 86 mbar at room temperature in 96% yield after stirring the reaction mixture for only 2 h at room temperature. The ^{29}Si NMR spectrum of silane **3** exhibits a quintet at $\delta = -13.8$ ppm with a ^2J(Si,F) coupling constant of 47.1 Hz.



Scheme 5. Synthesis of bis(pentafluoroethyl)dichlorosilane (**3**).

The good accessibility of dichlorosilane **3** in a multigram quantity is a prerequisite for the study of further chemical transformations. Difluorobis(pentafluoroethyl)silane (**4**) was obtained by stirring a slurry of antimony trifluoride in neat dichlorosilane **3** at room temperature (Scheme 6).[10c] After fractional condensation, difluorosilane **4** was isolated as a colorless liquid with a vapor pressure of 315 mbar at room temperature in 96% yield. The melting point of difluorosilane **4** was estimated to be about −135 °C. The ^{29}Si NMR spectrum of **4** reveals a triplet of quintets at $\delta = -59.3$ ppm with characteristic coupling constants of ^1J(Si,F) = 353 and ^2J(Si,F) = 45.6 Hz (Table 2).



Scheme 6. Synthesis of difluorosilane **4** (top) and silane **5** (bottom).

Reaction of **3** with a slight excess of tributyltin hydride selectively affords $(C_2F_5)_2SiH_2$ (**5**), which was separated from the reaction mixture by a fractional condensation in 99% yield. The product has a vapor pressure of 380 mbar at room temperature and melts at −95 °C. In the ^{29}Si NMR spectrum the product shows a triplet of quintets of septets splitting at $\delta = -40.6$ ppm with characteristic ^1J(Si,H), ^2J(Si,F), and ^3J(Si,F) couplings of 243, 35.3, and 1.2 Hz, respectively (Figure 1 and

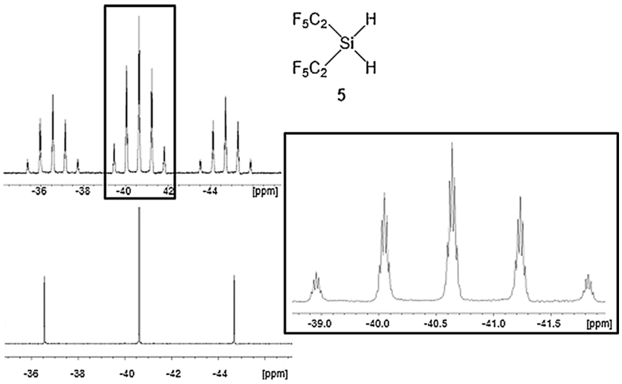


Figure 1. ^{29}Si^{19}F DEPT (top) and ^{29}Si{^{19}F} DEPT (bottom) NMR spectrum of bis(pentafluoroethyl)silane (**5**); right: detailed cut of the ^{29}Si^{19}F-DEPT NMR spectrum.

Table 2). The ^{19}F-decoupled ^{29}Si NMR spectrum exhibits a triplet due to the SiH coupling ($J = 243$ Hz) (Figure 1, bottom).

The molecular structures of silanes **4** and **5** were elucidated by in situ crystallization. This was achieved by first establishing a solid–liquid equilibrium just below the melting point inside a sealed capillary, then melting all the solid but for a tiny crystal seed (using a thin copper wire as an external heat source) followed by a slow chilling to the temperature of measurement at 100 K.

The Si–F bond lengths of **4** in the crystal (Figure 2) (155.9(1) and 155.4(1) pm) are in the expected range (*d*(Si–F): 156.7 pm in $(C_2F_5)_3SiF$,[8] *d*(S–F): 156 pm in SiF_4[11]). The F-Si-F angle of 110.9° is only slightly reduced in comparison to the C-Si-C angle of 108.1° and close to the ideal tetrahedral angle of 109.5° In contrast, the molecular structure of the dihydrosilane **5** (Figure 3) exhibits significantly different H-Si-H and C-Si-C angles of 113 and 103.0°, respectively. A large H-Si-H angle compared to a C-Si-C angle of two sterically demanding C_2F_5 groups[12] may surprise, but is consistent with BENT's rule.[13] The hydrogen substituents exhibit a lower electronegativity than the C_2F_5 groups. Hence they induce an increased s-orbital character in the Si–H bonds that affects a widening of the H-Si-H angle to 113°. As a consequence, the increased p-orbital character of the Si–C bonds compresses the C-Si-C angle to 103.0°.

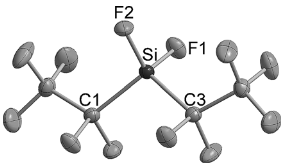


Figure 2. Molecular structure of $(C_2F_5)_2SiF_2$ (**4**); 50 % probability amplitude displacement ellipsoids are shown; selected bond lengths [pm] and angles [°]: Si–F1: 155.9(1), Si–F2: 155.4(1), Si–C1: 191.1(1), Si–C3: 191.0(1); C1-Si-C3: 108.1(1), F1-Si-F2: 110.9(1).

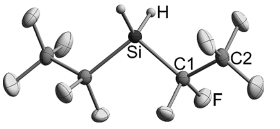
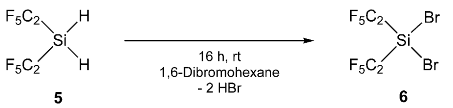


Figure 3. Molecular structure of $(C_2F_5)_2SiH_2$ (**5**); 50 % probability amplitude displacement ellipsoids are shown; selected bond lengths [pm] and angles [°]: Si–H1: 134(2), Si–C1: 192.8(1); C1-Si-C1′: 103.0(1), H1-Si-H1′: 113(2).

The protocol for the synthesis of $(C_2F_5)_2SiCl_2$ (**3**) cannot be extended to the corresponding dibromo derivative. Reaction of **2** with various acyl bromides invariantly led to intractable mixtures. In contrast to this, the reaction of **5** with a slight excess of bromine in 1,6-dibromohexane solution smoothly furnished product $(C_2F_5)_2SiBr_2$ in 93 % yield (Scheme 7).

After separation by fractional condensation, crude dibromobis(pentafluoroethyl)silane (**6**) was treated with mercury to remove traces of bromine. Finally, the product was isolated as a colorless liquid with a vapor pressure of 23 mbar at room temperature and a melting point of −90 °C. The ^{29}Si{^{19}F} DEPT NMR spectrum is characterized by a quintet at $\delta = -21.7$ ppm with a ^2J(Si,F) coupling constant of 47.8 Hz. In comparison to **4** and **5**, the molecular structure of $(C_2F_5)_2SiBr_2$ (**6**) (Figure 4) in the crystal exhibits a different conformer for the two pentafluoroethyl groups, presumably due to the obtuse C-Si-C angle of 114.1°. The Si–Br bond length of 215.4 pm is in the expected range of bromosilanes.[14]



Scheme 7. Synthesis of dibromosilane **6**.

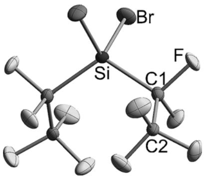


Figure 4. Molecular structure of **6**; 50 % probability amplitude displacement ellipsoids are shown; selected bond lengths [pm] and angles [°]: Si–Br1: 215.4(1), Si–C1: 192.6(5); C1-Si-C1′: 114.1(3), Br1-Si-Br1′: 113.4(1), Br1-Si-C1: 105.1(2)°.

IR spectroscopy

Figure 5 and Table 1 compile selected data of the IR data of silanes **3**–**6** in the gas phase. In Figure 2 relevant absorption bands are assigned to vibrational modes. Table 1 allows a comparison between measured and calculated data. The quantum chemical calculations were carried out with a DFT method on the B3LYP level employing the 6-311G(d,p) basis set.

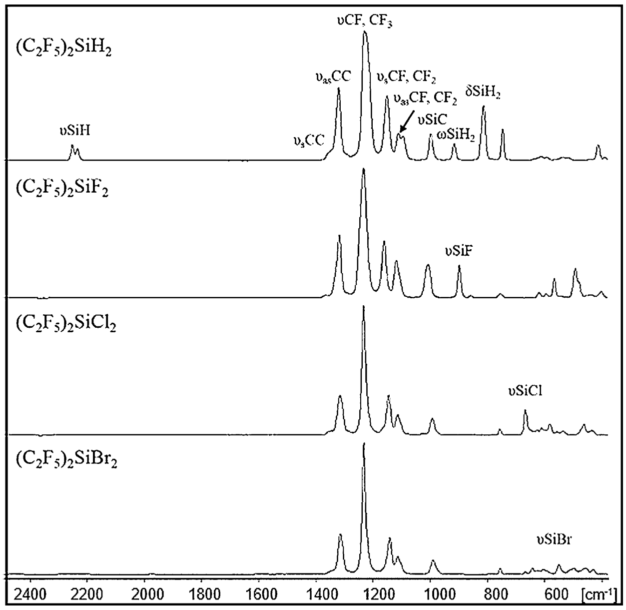


Figure 5. IR spectra of **5** (top), **4** (upper middle), **3** (lower middle), and **6** (bottom).

Table 1. Gas-phase IR data of the synthesized $(C_2F_5)_2SiX_2$ derivatives.[a]

R_2SiBr_2 Exptl.	Calcd[b]	R_2SiCl_2 Exptl.	Calcd[b]	R_2SiF_2 Exptl.	Calcd[b]	R_2SiH_2[c] Exptl.	Calcd[b]	Assignment
1332	1303	1342	1309	1362	1318	1351	1318	ν_sCC
1311	1297	1312	1295	1315	1302	1318	1306	ν_{as}CC
1229	1220/ 1208	1229	1225/ 1218	1230	1233/ 1223	1227	1223/ 1216	ν_{s+as}CF, CF_3
1137	1126	1142	1135	1158	1152	1147	1143	ν_sCF,CF_2
1110	1099	1111	1133	1116	1095	1108	1135	ν_{as}CF,CF_2
984	984/ 967	990	984/ 974	1004	997/ 993	995	994/ 979	ν_{as+s}SiC
746	746	753	746	753	740	743	739	δCF_3
545/ 492	524/ 483	607/ 577	597/ 566	1004/ 895	976/ 872	2249/ 2231	2304/ 2283	ν_{as+s}SiX

[a] Wavenumbers in cm^{-1}. [b] B3LYP/6-311G(d,p). [c] δSiH_2: 913, ωSiH_2: 810; calcd: 924, 811.

The vibrational bands at about 1300 cm^{-1} correspond to C–C stretching modes, whereby asymmetrical vibration is clearly more intensive than the symmetrical one. Apart from the Si–H bond of silane **5** this stretching mode exhibits the highest wavenumber. The most intensive bands are caused by the symmetrical and asymmetrical C–F stretching vibrations of the CF_3 groups at approximately 1220 cm^{-1}. Noticeably, the bands of the related vibrations of the CF_2 units are of lower intensity.

For the halogen-substituted silanes (X = F, Cl, Br) a clear trend is obtained. An increasing electronegativity of the halogen substituents leads to increasing energies for the characteristic vibrational modes. This is especially evident for the Si–X streching modes, but also applicable to the symmetric and antisymmetric CC–, as well as CF– valence modes of the pentafluoroethyl groups.

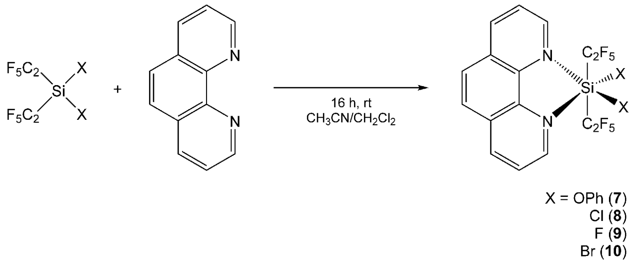
Bis(pentafluoroethyl)silane adducts with N bases

The silicon atom in bis(pentafluoroethyl)silanes is characterized by an inherently high Lewis acidity. Consistently, a wide variety of donor species forms adducts with these kinds of silanes. In general, such adducts are stable in the solid state and are isolated in good yields.[15] Kummer et al. investigated Lewis donor acceptor adducts of amine bases and different silane derivatives.[16] The complex stability of a silane adduct increases in the order pyridine < bipyridine < 1,10-phenanthroline. Keeping this in mind, we investigated the acceptor behavior of the synthesized silanes towards 1,10-phenanthroline.

Silanes **2**–**6** react with 1,10-phenanthroline in acetonitrile or dichloromethane within 1–3 h and the corresponding adducts **7**–**10** (Scheme 8) are formed in excellent yields. All adducts are moderately soluble in acetonitrile and nearly insoluble in dichloromethane, ethanol, and pentane.

NMR spectroscopy

For pentafluoroethyl-substituted silicon compounds shift ranges in ^{29}Si NMR spectra correlate nicely with the coordination number of the Si atom. The tetrahedrally coordinated silicon atoms in bis(pentafluoroethyl)silanes exhibit chemical shifts between $\delta = +10$ to -75 ppm. Coordination of a chelating phenanthroline ligand forming an octahedral silicate complex has an eminent influence on the ^{29}Si NMR chemical shift. These compounds reveal chemical shifts for the central silicon atoms below $\delta = -150$ ppm. The ^{19}F NMR resonances of the phenanthroline complexes are shifted downfield compared to the corresponding silanes. This effect is considerably more pronounced for the CF_2 groups than for the CF_3 groups. The ^2J(Si,F) coupling constants are comparable to those of the silanes and do not differ significantly. Comparison of the difluorosilane **4** and the corresponding phenanthroline adduct **9** reveals a peculiarity. The ^{19}F NMR resonance of the fluorine atoms directly connected to the silicon atom shift significantly ($\delta = -150.6$ (**4**) and -128.8 ppm (**9**)). Furthermore, the ^1J(Si,F) coupling constants decrease significantly from 353 (**4**) to 258 Hz (**9**). ^{1}H and ^{13}C NMR data are comparable to free 1,10-phenanthroline.



Scheme 8. Reaction of bis(pentafluoroethyl)silanes with 1,10-phenanthroline yielding the corresponding phenanthroline adducts.

Table 2 gives an overview of the characteristic NMR spectroscopic data collected for the synthesized bis(pentafluoroethyl)-silanes and their adducts with 1,10-phenanthroline.

Table 2. NMR data of $(C_2F_5)_2SiR_2$ and substrates.

		^{29}Si	^2J(Si,F)	$^{19}F(CF_3)$	$^{19}F(CF_2)$
$Cl_2Si(OPh)_2$	**1**	−63.3			
$(C_2F_5)_2Si(OPh)_2$[a]	**2**	−72.5	41.5	−82.9	−129.3
$(C_2F_5)_2SiCl_2$[a]	**3**	−14.0	45.3	−82.1	−127.4
$(C_2F_5)_2SiF_2$[a,b]	**4**	−59.3	46.3	−84.8	−132.4
$(C_2F_5)_2SiH_2$[a]	**5**	−40.6	34.3	−85.1	−124.4
$(C_2F_5)_2SiBr_2$[a]	**6**	−21.7	47.8	−81.0	−125.0
$[Si(C_2F_5)_2(OPh)_2(phen)]$[c]	**7**	−175.5	38.5	−81.3	−119.1
$[Si(C_2F_5)_2Cl_2(phen)]$[c]	**8**	−165.5	45.3	−80.1	−114.4
$[Si(C_2F_5)_2F_2(phen)]$[c,d]	**9**	−171.6	35.3	−82.7	−125.8
$[Si(C_2F_5)_2Br_2(phen)]$[c]	**10**	−179.7	50.2	−80.5	−112.5

[a] Neat compound. [b] $(C_2F_5)_2Si\mathbf{F_2}$: $\delta(^{19}\mathbf{F}\text{–Si}) = -150.6$ ppm, ^1J(Si,F) = 353 Hz. [c] In acetonitrile. [d] $[(C_2F_5)_2Si\mathbf{F_2}(phen)]$: $\delta(^{19}\mathbf{F}\text{–Si}) = -128.8$ ppm, ^1J(Si,F) = 258 Hz.

X-ray structure determination

Single crystals of the phenanthroline adducts were grown from cold acetonitrile solution or mixtures of acetonitrile and dichloromethane and analyzed by X-ray diffraction. The molecular structures are shown in Figures 6–8. The C_2F_5 groups ex-

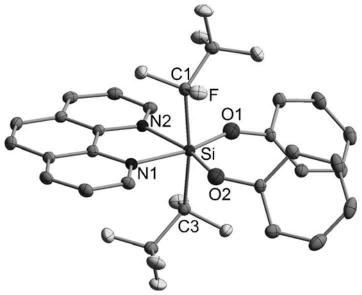


Figure 6. Molecular structure of $[Si(C_2F_5)_2(OPh)_2(phen)]$ (**7**); 50 % probability amplitude displacement ellipsoids are shown; H-atoms bonded to carbon omitted for clarity; selected bond lengths [pm] and angles [°]: Si–O1: 168.5(1), Si–O2: 169.2(1), Si–N1: 201.6(1), Si–N2: 202.9(1); N1-Si-N2: 79.1(1), O1-Si-O2 105.0(1).

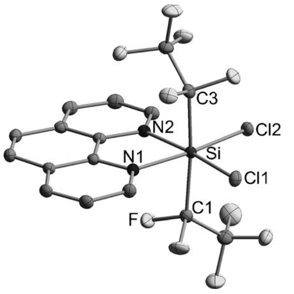


Figure 7. Molecular structure of $[Si(C_2F_5)_2Cl_2(phen)]$ (**8**) 50 % probability amplitude displacement ellipsoids are shown; H-atoms bonded to carbon omitted for clarity; selected bond lengths [pm] and angles [°]: Si–Cl1: 216.6(1), Si–Cl2: 215.3(1), Si–N1: 199.2(1), Si–N2: 200.3(1); N1-Si-N2: 81.0(1); Cl1-Si-Cl2: 94.2(1).

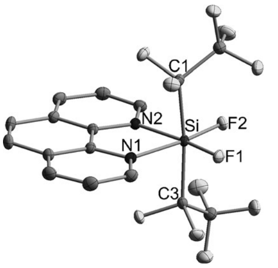


Figure 8. Molecular structure of $[Si(C_2F_5)_2F_2(phen)]$ (**9**); 50 % probability amplitude displacement ellipsoids are shown; H-atoms bonded to carbon omitted for clarity; selected bond lengths [pm] and angles [°]: Si–F1: 164.4(1), Si–F2: 164.2(1), Si–N1: 199.4(1), Si–N2: 198.9(1); N1-Si-N2: 80.6(1), F1-Si-F2: 98.1(1).

hibit a *trans* disposition at the six-coordinated Si atom. The two substituents X are *cis*-oriented in a joint plane with the chelating ligand. Whereas bond lengths and angles on the $Si(C_2F_5)_2$ axis are comparable, bond angles within the SiN_2X_2 unit differ considerably.

Dichlorosilane **3** reacts with trifluoroacetic acid forming bis(pentafluoroethyl)bis(trifluoroacetoxy)silane and HCl. After evaporation of the volatile compounds a colorless solid could be obtained that is highly sensitive towards moisture. The crude product is purified by sublimation at 20 °C and $1\cdot10^{-3}$ mbar. According to ^{13}C NMR spectra this product is a 1:2 complex of $(C_2F_5)_2Si(O_2CCF_3)_2$ and acetonitrile.

The ^{29}Si NMR spectrum of $[Si(C_2F_5)_2(O_2CCF_3)_2(NCCH_3)_2]$ (**11**) reveals a quintet at $\delta = -196.4$ ppm which is characteristic for an octahedrally coordinated silicon atom in bis(pentafluoroethyl)-silicon compounds with a $^2J(Si,F)$ coupling constant of 44 Hz. In the ^{19}F NMR spectrum, the fluorine atoms of the trifluoroacetoxy group ($\delta = -76.8$ ppm) are shifted downfield compared to the CF_3 groups of the pentafluoroethyl substituents ($\delta = -81.9$ ppm).

Vibrational spectroscopy confirms the synthesis of **11**. Characteristic vibrational modes for symmetrical and antisymmetrical carbon nitrogen stretching modes of the acetonitrile ligands show resonances at 2340 and 2311 cm^{-1}, respectively. Valence modes for the carbonyl functionality exhibit intensive vibrational bands at about 1767 cm^{-1}. The most intensive bands at 1149 and 1117 cm^{-1} are ascribable to the C–F vibrational modes of the CF_3 groups ($O_2CCF_3 + C_2F_5$) and the CF_2 groups (C_2F_5), respectively. Single crystals of **11** could be obtained from a dichloromethane solution at −28 °C (Figure 9). The solid-state structure of the acetonitrile adduct **11** reveals the picture of a slightly distorted octahedral structure with two pentafluoroethyl groups in *trans* position. In contrast to this, *cis* orientation of the trifluoroacetoxy and the trimethylcyanido ligands is preferred. The strong widening of the O1-Si-O1′ angle (101.1(2)°) is remarkable, but presumably may be due to the spatial demand of the trifluoroacetoxy groups.

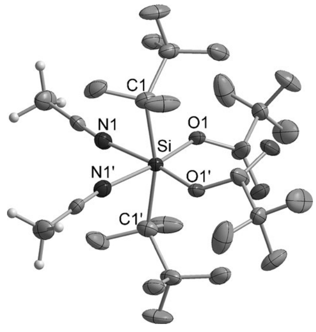


Figure 9. Molecular structure of $[Si(C_2F_5)_2(O_2CCF_3)_2(NCCH_3)_2]$ (**11**); 50 % probability amplitude displacement ellipsoids are shown; selected bond lengths [pm] and angles [°]: Si–O1: 173.0(3), Si–N1: 195.4(3); N1-Si-N1′: 87.4(2), C1-Si-C1′: 165.9(2), O1-Si-O1′: 101.1(2).

Conclusion

We have successfully devised a convenient protocol for the synthesis of bis(pentafluoroethyl)silanes on a multigram scale. A key step for this is the employment of $(PhO)_2SiCl_2$ in which the Lewis acidity of the Si centre is mitigated by the π-donating phenoxy groups. Consistently, the replacement of chlorine atoms by two C_2F_5 groups was smoothly effected without fluoride transfer from LiC_2F_5. The phenoxy groups are cleanly replaced by two chlorine atoms during reaction with carboxylic acid chlorides in the presence of a $FeCl_3$ catalyst. The substitution of the chlorides in $(C_2F_5)_2SiCl_2$ by various nucleophiles provides access to a plethora of bis(pentafluoroethyl)silanes. As the introduction of pentafluoroethyl functionalities into silicon compounds enhances the Lewis acidity of the resulting species, the synthesis of previously inaccessible hypervalent silicon derivatives is feasible. Due to the Lewis acidity, complex formation to a series of hexacoordinate adducts with 1,10-phenanthroline is rendered possible. The bonding situations in the novel compounds were elucidated by spectroscopic means and X-ray analyses.

Experimental Section

Materials and apparatus

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Chemicals were obtained from commercial sources and used without further purification. NMR spectra were recorded on a Bruker Avance III 300 spectrometer (^{29}Si: 59.6 MHz; ^{19}F: 282.4 MHz; ^{13}C: 75.5 MHz; ^{1}H: 300.1 MHz) with positive shifts being downfield from the external standards (TMS(^{29}Si), (^{13}C) and (^{1}H), and CCl_3F (^{19}F)). IR spectroscopic measurements were conducted on a Bruker Alpha-FTIR spectrometer. For liquids and solid-state materials we used an ATR element from Bruker; gas-phase spectra were collected using a teflon gas cell with KBr windows. EI mass spectra were recorded with a Micromass VG Autospec X magnetic sector mass spectrometer (20 eV) with a standard EI source. Volatile compounds were introduced by a gas-phase inlet. Intensities are referenced to the most intense peak of a group. C, H, N analyses were carried out with a HEKAtech Euro EA 3000 apparatus.

Synthetic methods

Synthesis of dichlorodiphenoxysilane[9] (1): A solution of silicon tetrachloride (93.3 g, 549 mmol) in diethyl ether (350 mL) was combined with a solution of phenol (108 g, 1.15 mol) in diethyl ether (200 mL) and the mixture was stirred at rt for 2 d. After evaporation of the solvent, **1** was obtained by vacuum distillation ($1\cdot10^{-3}$ mbar) at 100 °C as a colorless liquid in 73% yield (114 g, 401 mmol). ^{1}H NMR (300.13 MHz, neat, [D$_6$]acetone): $\delta=6.4$–6.6 ppm (m, Ph–H); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta=-63.3$ ppm (m, $Cl_2Si(OPh)_2$).

Synthesis of bis(pentafluoroethyl)diphenoxysilane (2): A 1.6 M n-butyllithium solution in *n*-hexane (129.07 g, 189.81 mL, 303.73 mmol) was dissolved in diethyl ether (350 mL) and degassed at −90 °C. The solution was stirred for 30 min at −85 °C in an atmosphere of C_2F_5H (313.70 mmol). While stirring for 30 min the temperature was slowly raised to −60 °C. After addition of dichlorodiphenoxysilane, $Cl_2Si(OPh)_2$, (**1**), (52.15 g, 151.9 mmol) at −60 °C, the mixture was warmed to rt and stirred overnight. A colorless precipitate was filtered off. After evaporation of the solvent, compound **2** was obtained by vacuum distillation ($1\cdot10^{-3}$ mbar) at 67 °C as a colorless liquid in 74% yield (51.07 g, 113.0 mmol). ^{1}H NMR (300.13 MHz, neat, [D$_6$]acetone): $\delta=6.7$ (m, 3H, *meta*-H, *para*-H), 6.8 (m, 2H, *ortho*-H); ^{13}C{^{1}H} NMR (75.47 MHz, neat, [D$_6$]acetone): $\delta=113.9$ (t, q, ^{1}J(C,F) = 275.7, ^{2}J(C,F) = 45.2 Hz, $-CF_2-$), 118.6 (s, *meta*-C), 118.9 (q, t, ^{1}J(C,F) = 284.9, ^{2}J(C,F) = 29.7 Hz, CF_3-), 124.1 (s, *para*-C), 129.4 (s, *ortho*-C), 150.8 ppm (s, *ipso*-C); ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta=-82.9$ (s, CF_3-), −129.3 ppm (s, $-CF_2-$); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta=-72.5$ ppm (quint, ^{2}J(Si,F) = 41.5 Hz, $(C_2F_5)_2Si(OPh)_2$); ^{29}Si{^{19}F} NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta=-72.5$ ppm (s, $(C_2F_5)_2Si(OPh)_2$).

Synthesis of dichlorobis(pentafluoroethyl)silane (3): The reaction was performed in a sealed ampoule. Phenylacetyl chloride (55.28 g, 357.6 mmol) was added to solid iron(III) chloride (248 mg, 1.53 mmol). After the addition of bis(pentafluoroethyl)diphenoxysilane (**2**) (24.20 g, 53.54 mmol), the degassed solution was stirred for 5 h at rt. Product **3** and other volatile components were separated under dynamic vacuum conditions by fractional condensation through two traps at −40 and −196 °C. The −196 °C trap contains **3** and HCl, which was separated at −100 °C. Compound **3** was obtained as a colorless liquid with a vapor pressure of 86 mbar at room temperature and a melting point of −135 °C in 96% yield (17.26 g, 51.39 mmol). ^{13}C{^{1}H} NMR (75.47 MHz, neat, [D$_6$]acetone): $\delta=113.2$ (t, q, ^{1}J(C,F) = 276.1, ^{2}J(C,F) = 43.1 Hz, $-CF_2-$), 118.9 ppm (q, t, ^{1}J(C,F) = 285.1, ^{2}J(C,F) = 29.6 Hz, CF_3-); ^{13}C{^{19}F} NMR (75.47 MHz, neat, [D$_6$]acetone): $\delta=113.2$ (s, $-CF_2-$), 118.9 ppm (s, CF_3-); ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta=-82.1$ (s, CF_3-), −127.4 ppm (s, $-CF_2-$); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta=-13.8$ ppm (quint, ^{2}J(Si,F) = 47.1 Hz, $(C_2F_5)_2SiCl_2$); ^{29}Si{^{19}F} NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta=-13.8$ ppm (s, $(C_2F_5)_2SiCl_2$); IR (gas phase): $\tilde{\nu}=1342$ (w, ν_s(CC), C_2F_5), 1312 (m, ν_{as}(CC), C_2F_5), 1232 (s, ν_{s+as}(CF), CF_3), 1142 (m, ν_s(CF), CF_2), 1111 (m, ν_{as}(CF), CF_2), 990 (m, ν_{as+s}(SiC)), 753 (w, $\delta(CF_3)$), 664 (m, ν_{as}(SiCl)), 623 (w, $\delta(CF_2)+\nu_s$(SiCl)), 607 (w, $\delta(CF_2)+\nu_{as}$(SiCl)), 577 (w, ν_s(SiCl)), 459 cm^{-1} (w, δ(SiCl)).

Synthesis of difluorobis(pentafluoroethyl)silane (4): In a sealed ampoule antimony trifluoride (5.34 g, 30.0 mmol) was stirred for 90 min at rt in an atmosphere of bis(pentafluoroethyl)dichlorosilane (3.37 g, 10.0 mmol). Product **4** was separated under dynamic vacuum conditions by fractional condensation through two traps at −60 and −196 °C. The −196 °C trap contains difluorosilane **4**, which was obtained as a colorless liquid with a vapor pressure of 315 mbar at room temperature in 97% yield (2.95 g, 9.70 mmol). M.p. −135 °C; ^{13}C{^{19}F} NMR (75.47 MHz, neat, [D$_6$]acetone): $\delta=112.3$ (s, $-CF_2-$), 118.4 ppm (s, CF_3-); ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta=-84.7$ (s, CF_3-), −132.5 (s, $-CF_2-$), −150.5 ppm (s, SiF_2); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta=-59.3$ (t, quint, ^{1}J(Si,F) = 352.9, ^{2}J(Si,F) = 45.6 Hz, $(C_2F_5)_2SiF_2$); IR (gas phase): $\tilde{\nu}=1362$ (w, ν_s(CC), C_2F_5), 1315 (s, ν_{as}(CC), C_2F_5), 1230 (vs, ν_{s+as}(CF), CF_3), 1158 (s, ν_s(CF), CF_2), 1116 (m, ν_{as}(CF), CF_2), 1004 (m, ν_{as+s}(SiC)), 895 (m, ν_s(SiF)), 855 (w), 753 (w, $\delta(CF_3)$), 616 (w, $\delta(CF_2)$), 590 (w, $\delta(CF_3)$), 562 (w), 489 (w, δ(SiF)), 398 cm^{-1} (w, δ(SiF)).

Synthesis of bis(pentafluoroethyl)silane (5): In a sealed ampoule bis(pentafluoroethyl)dichlorosilane (**3**) (4.64 g, 17.3 mmol) was condensed to a degassed solution of tributyltin hydride (11.3 g, 38.9 mmol). The mixture was stirred for 17 h at rt. Product **5** and other volatile components were separated under dynamic vacuum conditions by fractional condensation through two traps at −65 and −196 °C. The −196 °C trap contains product **5**, which was obtained as a colorless liquid in 99% yield (4.73 g, 17.1 mmol). Vapor pressure: 380 mbar (rt); m.p. −95 °C; ^{1}H NMR (300.13 MHz, neat, [D$_6$]acetone): $\delta=4.8$ ppm (m, SiH_2); ^{13}C{^{19}F} NMR (75.47 MHz, neat, [D$_6$]acetone): $\delta=116.5$ (t, ^{2}J(C,H) = 7.4, ^{1}J(C,Si) = 74.5 Hz, $-CF_2-$), 119.4 ppm (s, ^{2}J(C,Si) = 7.4 Hz, CF_3-); ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta=-82.1$ ppm (s, ^{1}J(F,C) = 279.4 Hz, CF_3-), −124.5 ppm (t, ^{2}J(F,H) = 9.7, ^{1}J(F,C) = 270.7 Hz, $-CF_2-$); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta=-40.6$ ppm (t, quint, sept, ^{1}J(Si,H) = 242.9, ^{2}J(Si,F) = 35.3, ^{3}J(Si,F) = 1.2 Hz, $(C_2F_5)_2SiH_2$); ^{29}Si{^{19}F} NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta=-40.6$ ppm (t, ^{1}J(Si,H) = 242.9, ^{1}J(Si,C) = 74.5, ^{2}J(Si,C) = 7.2 Hz, $(C_2F_5)_2SiH_2$); IR (gas phase): $\tilde{\nu}=2249$ (m, ν_{as}(SiH)), 2231 (m, ν_s(SiH)), 1351 (w, ν_s(CC)), 1318 (s, ν_{as}(CC)), 1227 (vs, ν_{s+as}(CF), CF_3), 1147 (s, ν_s(CF), CF_2), 1108 (m, ν_{as}(CF), CF_2), 1092 (m, ν_{as}(CF), CF_2), 995 (m, ν_{s+as}(SiC)), 913 (m, δ(SiH_2)), 810 (s, δ(SiH_2)), 743 (m, δ(CF_3)), 608 (w, δ(CF_2) + δ(SiH)), 590 (w, δ(CF_2)), 533 (w, δ(CF_3)), 515 (w, δ(SiH)), 409 (w), 385 cm^{-1} (m).

Synthesis of dibromobis(pentafluoroethyl)silane (6): In a sealed ampoule bromine (3.1 mL, 59.3 mmol) was dissolved in 1,6-dibromohexane (35 mL). After degassing, bis(pentafluoroethyl)silane (**5**) (6.48 g, 24.2 mmol) was condensed onto the solution. The reaction mixture was slowly warmed to rt and stirred for 16 h. Evaporated HBr was separated in a trap at −65 °C. Remaining volatile compounds were condensed onto elemental mercury and stirred for 1 h at room temperature. The pure product was isolated from mercury and mercury salts via condensation. Silane **6** was obtained in 93 % yield (9.49 g, 22.4 mmol); Vapor pressure: 28 mbar (rt); m.p. −90 °C; ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta = -81.0$ (s, CF_3–), −125.0 ppm (s, –CF_2–); ^{29}Si{^{19}F} NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta = -21.7$ ppm (quint., ^2J(Si,F) = 47.8 Hz, $(C_2F_5)_2SiBr_2$); IR (gas phase): $\tilde{\nu} = 1332$ (w, ν_s(CC), C_2F_5), 1311 (s, ν_{as}(CC), C_2F_5), 1229 (vs, ν_{s+as}(CF), CF_3), 1137 (s, ν_s(CF), CF_2), 1110 (m, ν_{as}(CF), CF_2), 984 (m, ν_{s+as}(SiC)), 895 (vw), 752 (w, δ(CF_3)), 622 (w, δ(CF_2)), 591 (w, δ(CF_3)), 545 (m, ν_{as}(SiBr)), 492 (m, ν_s(SiBr)), 459 (w, δ(SiBr)), 447 (w, δ(C_2F_5)), 426 cm^{-1} (w, δ(C_2F_5)).

Synthesis of [Si(C_2F_5)$_2$(OPh)$_2$(phen)] (7): Bis(pentafluoroethyl)-diphenoxysilane (**2**) (1.40 g, 3.09 mmol) was added to a solution of 1,10-phenanthroline (0.56 g, 3.10 mmol) in acetonitrile (8 mL). After the mixture had been stirred for 3 h at rt, solvents were removed under reduced pressure. Pure product **7** was obtained after recrystallization from acetonitrile (4 mL) at −28 °C as a yellow solid in 91 % yield (1.78 g, 2.81 mmol). ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta = -81.3$ (s, CF_3–), −119.1 ppm (s, –CF_2–); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta = -178.5$ ppm (quint, ^2J(Si,F) = 38.5 Hz, $(C_2F_5)_2Si(OPh)_2$(phen)); ^{29}Si{^{19}F} NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta = -178.5$ ppm (s, $(C_2F_5)_2Si(OPh)_2$(phen)); elemental analysis calcd (%) for $C_{28}H_{18}F_{10}N_2O_2Si$ ($M = 633.52$): C 53.17, H 2.87, N 4.43; found: C 52.82, H 2.91, N 4.33; IR (ATR): $\tilde{\nu} = 3113$ (vw, ν(CH)), 1597 (m, ν(C=C), phen), 1586 (m, ν(C=C), phen), 1526 (m, ν(C=N) + ν(C=C)), 1438 (m, δ(CH)), 1307 (m, ν_s(CC), C_2F_5), 1295 (m, ν_{as}(CC), C_2F_5), 1198 (s, ν(CF), CF_3), 1177 (s, ν(CF), CF_3), 1117 (s, ν_{as}(CF), CF_2), 1028 (s, ν_s(CF), CF_2), 952 (m, ν_{as}(SiC)), 944 (m, ν_s(SiC)), 931 (w, ν(SiO)), 912 (w, ν(SiO)), 734 (m, δ(CF_3)), 724 (w, ν(SiO)), 564 (w, δ(C_2F_5)), 432 cm^{-1} (w).

Synthesis of [Si(C_2F_5)$_2$Cl$_2$(phen)] (8): Dichlorobis(pentafluoroethyl)-silane (**3**) (668 mg, 2.20 mmol) was condensed onto a degassed solution of 1,10-phenanthroline (360 mg, 1.99 mmol) in acetonitrile (8 mL). After the mixture had been stirred for 1 h at rt, acetonitrile was removed under reduced pressure. The product **8** was obtained after recrystallization from acetonitrile (2 mL) at −28 °C as a colorless solid in 59 % yield (530 mg, 1.17 mmol); ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta = -79.9$ (s, CF_3–), −114.1 ppm (s, –CF_2–); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta = -165.5$ ppm (quint, ^2J(Si,F) = 45.3 Hz, $(C_2F_5)_2SiCl_2$(phen)); ^{29}Si{^{19}F} NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta = -165.5$ ppm (s, $(C_2F_5)_2SiCl_2$(phen)); elemental analysis calcd (%) for $C_{16}H_8Cl_2F_{10}N_2Si$ ($M = 517.22$): C 37.10, H 1.56, N 5.42; found: C 37.24, H 1.62, N 5.51; IR (ATR): $\tilde{\nu} = 3108$ (vw, ν(CH)), 1619 (w, ν(C=C)), 1586 (w, ν(C=N) + ν(C=C)), 1432 (m, δ(CH)), 1293 (m, b, ν(CC), C_2F_5), 1207 (s, ν_{as}(CF), CF_3), 1168 (vs, ν_s(CF), CF_3), 1098 (s, ν_{as}(CF), CF_2), 1024 (s, ν_s(CF), CF_2), 747 (s, δ(CF_3)), 564 (s, δ(C_2F_5)), 418 cm^{-1} (w).

Synthesis of [Si(C_2F_5)$_2$F$_2$(phen)] (9): Bis(pentafluoroethyl)difluorosilane (**4**) (435 mg, 1.43 mmol) was condensed at −196 °C onto a degassed solution of 1,10-phenanthroline (230 mg, 1.27 mmol) in acetonitrile (6 mL). After the mixture had been stirred for 20 h at rt, acetonitrile was removed under reduced pressure. Product **9** was obtained after recrystallization from acetonitrile (2 mL) at −28 °C as a colorless solid in 28 % yield (0.17 g, 0.35 mmol). ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta = -80.1$ (m, CF_3–), −126.0 (m, –CF_2–), −129.1 ppm (m, –SiF_2); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta = -170.9$ ppm (t, quint, ^1J(Si,F) = 257.7, ^2J(Si,F) = 36.5 Hz, $(C_2F_5)_2SiF$(phen)); ^{29}Si{^{19}F} NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta = -170.9$ (s, $(C_2F_5)_2SiF_2$(phen)); elemental analysis calcd (%) for $C_{16}H_8F_{12}N_2Si$ ($M = 484.03$): C 39.68, H 1.66, N 5.78; found: C 39.37, H 1.72, N 5.83; IR (ATR): $\tilde{\nu} = 3112$ (vw, ν(CH)), 1622 (w, ν(C=C)), 1584 (w, ν(C=N) + ν(C=C)), 1530 (w, δ(CH)), 1438 (m, δ(CH)), 1323 (m, ν_s(CC), C_2F_5), 1307 (m, ν_{as}(CC), C_2F_5), 1198 (s, ν(CF), CF_3), 1177 (s, ν(CF), CF_3), 1151 (s, δ(CH)), 1117 (s, ν_{as}(SiC)), 1109 (s, ν_s(SiC)), 1028 (s, ν(CF), CF_2), 955 (m, ν_s(CC), C_2F_5), 947 (m, ν_s(CC), C_2F_5), 880 (m, δ(C=C) + δ(CH)), 856 (s, δ(CH)), 771 (s, ν(SiF)), 756 (s, δ(CH)), 724 (vs, δ(C_2F_5)), 564 (s), 528 (m, δ(C_2F_5)), 488 (s), 452 (m), 432 (s), 404 cm^{-1} (w, δ(SiF).

Synthesis of [Si(C_2F_5)$_2$Br$_2$(phen)] (10): 1,10-Phenanthroline (155 mg, 0.86 mmol) was dissolved in dry dichloromethane. The colorless solution was degassed and treated with dibromobis(pentafluoroethyl)silane (**6**) (373 mg, 0.88 mmol) resulting in a colorless suspension that was stirred for 3 h at rt. After evaporation of the solvent, dry ethanol was condensed to the colorless solid to remove unreacted 1,10-phenanthroline. After filtration the product was obtained as a colorless solid in 55 % yield (287 mg, 0.47 mmol). ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta = -79.7$ (s, CF_3–), −111.7 ppm (s, –CF_2–); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta = -179.7$ ppm (quin, ^2J(Si,F) = 50.4 Hz, $(C_2F_5)_2SiBr_2$(phen)); elemental analysis calcd (%) for $C_{16}H_8Br_2F_{10}N_2Si$ ($M = 606.13$): C 31.70, H 1.33, N 4.62, Br 26.37; found: C 34.02, H 1.97, N 4.97; IR (ATR): $\tilde{\nu} = 3098$ (w, ν(CH)), 2924 (w, ν(CH)), 2853 (w, ν(CH)), 1618 (w, ν(C=C)), 1585 (w, ν(C=N) + ν(C=C)), 1527 (m, δ(CH)), 1494 (w, δ(CH)), 1430 (m, ν(C=C) + δ(CH)), 1297 (m, ν_s(CC), C_2F_5), 1284 (m, ν_{as}(CC), C_2F_5), 1210 (m, ν_s(CF), CF_3), 1168 (vs, ν_{as}(CF), CF_3), 1099 (s, ν_{as}(CF), CF_3), 1037 (s, ν_s(CF), CF_2), 963 (s, δ(CF_2)), 935 (w), 875 (m, δ(C=C)), 848 (s, δ(CH)), 780 (w), 745 (m, δ(CH)), 720 (s, δ(CF_3)), 645 (m, δ(C=C)), 615 (m, δ(C_2F_5)), 589 (m, δ(C_2F_5)), 545 (m, δ(SiN)), 472 (s), 457 (s), 434 (s), 422 (s), 404 (vs, ν_s(SiBr)), 389 cm^{-1} (vs, ν_{as}(SiBr)).

Synthesis of [Si(C_2F_5)$_2$(O$_2$CCF$_3$)$_2$(NCCH$_3$)$_2$] (11): A mixture of trifluoroacetic anhydride and trifluoroacetic acid (474 mg, 4.16 mmol) was dissolved in acetonitrile (15 mL). Dichlorobis(pentafluoroethyl)-silane, **3**, (682 mg, 2.03 mmol) was condensed onto the solution and warmed to rt while stirring. After evaporation of the volatile compounds, a colorless solid was obtained. Sublimation gave the product in 70 % yield (816 mg, 1.42 mmol). ^{19}F NMR (282.40 MHz, neat, [D$_6$]acetone): $\delta = -76.8$ (s, –O_2CCF_3), −81.9 (s, –CF_3), −123.6 ppm (s, –CF_2–); ^{29}Si NMR (59.63 Hz, neat, [D$_6$]acetone): $\delta = -196.4$ ppm (quin, ^2J(Si,F) = 44 Hz, $[Si(C_2F_5)_2(O_2CCF_3)_2(NCCH_3)_2]$); IR (ATR): $\tilde{\nu} = 3015$ (vw, ν(CH_3)), 2944 (w, ν(CH_3)), 2340 (m, ν_s(C≡N)), 2311 (w, ν_{as}(C≡N)), 1767 (s, $\nu_{as} + \nu_s$(C=O)), 1398 (m, ν_s(C-C), TFA + δ(CH_3)), 1386 ((m, ν_{as}(C–C), TFA + δ(CH_3)), 1306 (m, $\nu_s + \nu_{as}$(C–C), C_2F_5), 1181 (s, ν_s(CF), CF_3), 1149 (vs, ν(CF), CF_3, TFA + ν(CF), CF_3, C_2F_5), 1117 (vs, $\nu_s + \nu_{as}$(CF), CF_2), 1053 (s, ν(CF), CF_2 + δ(CH_3)), 968 (m, ν_{as}(SiC) + ν_s(C=O)), 858 (m, δ(CO_2)), 777 (w), 751 (w), 725 (w), 610 (m), 557 (s), 483 (m), 428 (s), 402 cm^{-1} (m).

X-ray structure determination

Solid-state structures of the highly volatile liquids were obtained by in situ crystallization. The structures were solved by direct methods and refined by full-matrix least squares cycles.[17] Data were corrected for Lorentz and polarization effects. Structure solution and refinement were carried out using the programs Olex2,[18] SHELX-97,[17] and Superflip.[19]

CCDC 1448711–1448717 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre

Acknowledgements

Financial support by the Merck KGaA (Darmstadt, Germany) is gratefully acknowledged. We thank Solvay (Hannover, Germany) for donation of pentafluoroethane (Solkane® 125). We are thankful to Dr. N. Ignatiev (Merck KGaA), Prof. Dr. L. Weber and Dr. J. Bader for helpful discussions. Furthermore, we acknowledge support by the Deutsche Forschungsgemeinschaft (Core Facility GED@BI, Mi477/21-1).

Keywords: fluorine · halogens · Lewis acids · perfluoroalkyl · silicon

[1] S. Steinhauer, T. Böttcher, N. Schwarze, B. Neumann, H.-G. Stammler, B. Hoge, *Angew. Chem. Int. Ed.* **2014**, *53*, 13269 – 13272; *Angew. Chem.* **2014**, *126*, 13485 – 13488.

[2] N. Schwarze, S. Steinhauer, B. Neumann, H.-G. Stammler, B. Hoge, *Angew. Chem.* **2016**, in preparation.

[3] N. Schwarze, S. Steinhauer, B. Neumann, H.-G. Stammler, B. Hoge, *Angew. Chem.* **2016**, in preparation.

[4] N. V. Ignat'ev, J. Bader, K. Koppe, B. Hoge, H. Willner, *J. Fluorine Chem.* **2015**, *171*, 36 – 45.

[5] H. Beckers, *Dissertation*, Wuppertal, **1987**.

[6] a) M. Heinrich, A. Marhold, A. Kolomeitsev, A. Kadyrov, G.- V. Röschenthaler, J. Barten (Bayer AG), DE 10128703 A 1, **2001**; b) M. H. Königsmann, Dissertation, Universität Bremen, **2005**; c) N. E. Shevchenko, V. G. Nenajdenko, G.-V. Röschenthaler, *J. Fluorine Chem.* **2008**, *129*, 390 – 396; d) B. Waerder, S. Steinhauer, B. Neumann, H.-G. Stammler, A. Mix, Y. V. Vishnevskiy, B. Hoge, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2014**, *53*, 11640 – 11644; *Angew. Chem.* **2014**, *126*, 11824 – 11828.

[7] a) S. Steinhauer, H.-G. Stammler, B. Neumann, N. Ignat'ev, B. Hoge, *Angew. Chem. Int. Ed.* **2014**, *53*, 562 – 564; *Angew. Chem.* **2014**, *126*, 573 – 575; b) N. Ignat'ev, M. Schulte, B. Hoge, S. Steinhauer, (Merck Patent GmbH), DE 102012006896A1, **2012**; c) B. Hoge, N. Ignat'ev, M. Schulte, S. Steinhauer, (BASF SE), WO 2013\150448A1, **2013**.

[8] a) S. Steinhauer, J. Bader, H.-G. Stammler, N. Ignat'ev, B. Hoge, *Angew. Chem. Int. Ed.* **2014**, *53*, 5206 – 5209; *Angew. Chem.* **2014**, *126*, 5307 – 5310.

[9] R. A. Thompson, F. S. Kipping, *J. Chem. Soc.* **1929**, 1179 – 1179.

[10] a) A. L. Narkon, V. I. Bakhmutov, S. A. Karapet'yan, A. I. Kalachev, P. M. Valetskii, G. M. Tseitlin, *Izvestiya Akademii Nauk SSSR Seriya Khimicheskaya* **1979**, *5*, 1090 – 1093; b) A. Corma, H. García, *Chem. Rev.* **2003**, *103*, 4307 – 4365; c) H. J. Frohn, M. Giesen, A. Klose, A. Lewin, V. V. Bardin, *J. Organomet. Chem.* **1996**, *506*, 155 – 164.

[11] M. Atoji, W. N. Lipscomb, *Acta Crystallogr.* **1954**, *7*, 597.

[12] A. V. Zakharov, Y. V. Vishnevskiy, N. Allefeld, J. Bader, B. Kurscheid, S. Steinhauer, B. Hoge, B. Neumann, H.-G. Stammler, R. J. F. Berger, N. W. Mitzel, *Eur. J. Inorg. Chem.* **2013**, 3392 – 3404.

[13] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275 – 311.

[14] J. Huheey, E. Keiter, R. Keiter, Anorganische Chemie Prinzipien von Struktur und Reaktivität, W. de Gruyter, 3. Aufl., **2003**.

[15] G. W. Fester, J. Eckstein, D. Gerlach, J. Wagler, E. Brendler, E. Kroke, *Inorg. Chem.* **2010**, *49*, 2667 – 2673.

[16] D. Kummer, A. Balkir, H. Köster, *J. Organomet. Chem.* **1979**, *178*, 29 – 54.

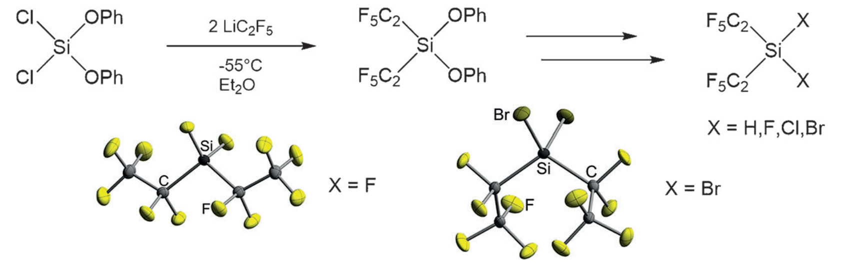
[17] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122.

[18] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339 – 341.

[19] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786 – 790.

Received: July 20, 2016

FULL PAPER



Hypervalent silicon: The introduction of pentafluoroethyl functionalities into silicon compounds enhances the Lewis acidity of the resulting species, which enables the synthesis of previously inaccessible hypervalent silicon derivatives. A convenient protocol for the selective synthesis of functional bis(pentafluoroethyl)silicon compounds is presented (see scheme).

Silicon Chemistry

*N. Schwarze, B. Kurscheid, S. Steinhauer, B. Neumann, H.-G. Stammler, N. Ignat'ev, B. Hoge**

■■ – ■■

Synthesis of Functional Bis(pentafluoroethyl)silanes $(C_2F_5)_2SiX_2$, with X = H, F, Cl, Br, OPh, and O_2CCF_3