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Fluoride complexation by bidentate silicon Lewis acids[†]

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Diethynyldiphenylsilane (**1**) and divinyldiphenylsilane (**2**) were functionalized by hydrosilylation reactions with HSiMe₂Cl, HSiMeCl₂ and HSiCl₃. Fluorination of the resulting compounds generates bidentate openchain Lewis acids of increasing acidity. All semi-flexible [Ph₂Si(CH=CHSiF_nMe_{3-n})₂ (n = 1, 2, 3)] and flexible [Ph₂Si(CH₂-CH₂SiF_nMe_{3-n})₂ (n = 1, 2, 3)] bidentate Lewis acids were obtained in good to excellent yields. The different fluoride ion complexation behavior was explored in detail by multinuclear (low temperature) NMR spectroscopy. The Lewis acidic bidentate molecules as well as the resulting mono- and bissilicates were completely characterized by NMR spectroscopy, mass spectrometry and in part by elemental analysis and X-ray diffraction experiments.

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Introduction

Self-organization and alignment of small molecular guests with large molecular hosts is an important field of supramolecular chemistry and termed host-guest chemistry. On the basis of Lewis acid-base-adduct formation there are two kinds of host-guest chemistry. One is a Lewis basic host coordinating a Lewis acidic guest, the other inverse system is a Lewis acidic host interacting with a Lewis basic guest.

Typical Lewis basic hosts are known since Pedersen reported the synthesis of crown ethers in 1967,¹ but in principle every multidentate ligand coordinating a metal cation can be regarded as Lewis basic host system. The reverse situation, Lewis acidic hosts containing multiple Lewis acidic atoms, are known as poly-Lewis acids.² They are capable of complexing anions as guest species.3 Many Lewis acidic fluoride receptors based on boron, mercury, tellurium and antimony were reported by Gabbaï and coworkers over the last twenty years.⁴ Group 14 elements have also been used to construct silicon-, germaniumand tin-based neutral anion receptors in cyclic or open-chain systems.^{2a,3,5-13} Prominent examples for group 14 based receptors are the fluorinated trisilacyclohexane derivatives of Brondani et al.,⁵ a 12-silacrown-3 reported by Jung and Xia,⁶ the ortho-bis(fluorosilyl)benzenes of Ito et al.,7 1,8-digermacyclotetradecane derivatives reported by Takeuchi et al.8 and several

Herein we report efficient syntheses of bidentate fluorosilanes with flexible (ethylene) and more rigid (vinylene) side arms by hydrosilylation of divinyldiphenylsilane and diethynyldiphenylsilane and subsequent fluorination reactions. The bidentate Lewis acidic hosts were converted with one or two equivalents of fluoride ions as guests using potassium fluoride and 18-crown-6 or [2.2.2]cryptand. We studied the behavior towards fluoride ions by NMR spectroscopy and X-ray diffraction.

Results and discussion

The organic frameworks diethynyldiphenylsilane (1) and divinyldiphenylsilane (2) were used to generate bidentate poly-

tin-containing ferrocenophanes of Jurkschat et al.9 Most of the bidentate group 14 based Lewis acids have 1,2-benzene^{7,10,11} or 1,8-naphtalene^{11,12} backbones, which sterically force anions between the acidic functions under formation of five- or sixmembered rings. Most recently, Jurkschat and co-workers have reported the synthesis of bifunctional Lewis acids containing silicon and tin atoms and their complexation behavior towards halide anions.¹⁴ These open-chain compounds exhibit two Lewis acidic tin atoms flexibly connected to a silicon atom by methylene groups enabling to capture halide anions between the tin atoms. To our knowledge there are no reports on Lewis acidic silicon atoms integrated into a flexible open-chain motif or any investigations of their behavior towards different host guest stoichiometries, i.e. more than one equivalent of halide anions. During our investigations in the field of poly-Lewis acids with rigid organic frameworks,2,15,16 we became interested in poly-Lewis acids with higher flexibility¹⁷ and their behavior and selectivity towards halide anion complexation phenomena.

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Scheme 1 Syntheses of 1 and 2 *via* salt elimination reactions. Reagents and conditions: (i) (a) $HC \equiv CMgBr$, THF, 0 °C – reflux, 12 h, 91%; (b) acetylene, *n*-BuLi, THF, -30 °C – rt., 8 h, 70%; (ii) $CH_2 \equiv CHMgCl$, THF, 0 °C – reflux, 12 h, 92%.

Lewis acids.¹⁸ Silane **1** was prepared by salt elimination reaction of dichlorodiphenylsilane with the commercially available ethynylmagnesium bromide (Scheme 1).¹⁹

Compound **1** was purified by short-path distillation, compound **2** by distillation. **1** crystallized in pure form. Their identity was confirmed by NMR spectroscopy, mass spectrometry and – in the case of **1** – by X-ray diffraction experiments. The crystal belongs to the monoclinic system, space group $P2_1/c$, with four molecules per unit cell (Fig. 1).

The coordination geometry at the silicon atom is almost tetrahedral [angles from 105.6(1)°, C(3)–Si(1)–C(5), to 114.2(1)° C(11)–Si(1)–C(5)]. The distances Si(1)–C(11) and Si(1)–C(5) are in a normal range for Si–C bonds, the distances Si(1)–C(1) and Si(1)–C(3) (1.825(1) and 1.837(1) Å) are both longer than the sum of the covalent radii of Si and C atoms.²⁰ The bonds C(1)–C(2) and C(3)–C(4) (1.192(2) and 1.196(2) Å) are of typical length for terminal C=C triple bonds.²¹

Divinyldiphenylsilane (2) was prepared by reacting dichlorodiphenylsilane with vinylmagnesium chloride in a salt elimin-



Fig. 1 Molecular structure of diethynyldiphenylsilane (1) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Phenyl hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)–C(1) 1.825(1), Si(1)–C(3) 1.837(1), Si(1)–C(5) 1.864(1), Si(1)–C(11) 1.852(1), C(1)–C(2) 1.192(2), C(3)–C(4) 1.196(2);C(1)–Si(1)– C(3) 108.9(1), C(1)–Si(1)–C(5) 108.3(1), C(1)–Si(1)–C(11) 110.7(1), C(3)–Si(1)– C(5) 105.6(1), C(3)–Si(1)–C(11) 108.9(1), C(11)–Si(1)–C(5) 114.2(1), C(2)–C(1)–Si(1) 177.5(1), C(4)–C(3)–Si(1) 175.0(1).

ation reaction (Scheme 1). Three doublets of doublets in the ¹H NMR spectrum with three different coupling constants of ${}^{3}J_{\rm H,H} = 20.3$ Hz, ${}^{3}J_{\rm H,H} = 14.6$ Hz and ${}^{2}J_{\rm H,H} = 3.7$ Hz are characterristic for the terminal vinyl substituents of silane 2.¹⁸

Hydrosilylation reactions

The unsaturated silanes 1 and 2 were converted into terminally silylated species with SiClMe₂, SiCl₂Me and SiCl₃ groups in hydrosilylation reactions (Scheme 2).^{2,15a,17}

All products were obtained in nearly quantitative yields (>97%) and characterized by multinuclear NMR spectroscopy. The less flexible (unsaturated) chlorosilanes **3**, **4** and **5** were isolated as colorless solids while all flexible (saturated) chlorosilanes **6**, **7** and **8** are colorless highly viscous liquids. Selected ¹H and ²⁹Si NMR chemical shifts of the unsaturated chlorosilanes **3**, **4** and **5** in CDCl₃ at ambient temperature are listed in Table **1**. In all three cases, the C=C double bond is selectively *trans*-substituted as it is indicated by the high coupling constant of the vinylic proton resonances (~22 Hz). The hydrosilylation reactions of **2** must be carried out in Et₂O to avoid the formation of the Markovnikov product.

The ¹³C{¹H} NMR spectra show the anticipated number of resonances. In all cases, the resonance of the olefinic carbon atom connected to the central silicon atom [δ = 152.1 (3), 150.2 (4) and 152.7 ppm (5)] is remarkably downfield shifted compared to the adjacent carbon atom [δ = 147.3 (3), 148.2 (4) and 145.1 ppm (5)].

Selected ¹H and ²⁹Si NMR chemical shifts of the saturated chlorosilanes **6**, **7** and **8** in CDCl₃ at ambient temperature are listed in Table 2. The gap in chemical shift between the multiplets of the methylene groups in the ¹H NMR spectra decreases with increasing the Lewis acidity of the chlorosilyl group from **6** to **8**. Surprisingly, **8** only shows a broadened singlet for both methylene groups.

The EI mass spectra of all saturated species do hardly show a molecular ion peak. All fragmentation patterns indicate the



Scheme 2 Syntheses of **3–8** *via* hydrosilylation of **1** and **2**. Reagents and conditions: (i) $\text{HSiCl}_n\text{Me}_{(3-n)}$, Karstedt's catalyst, rt., 2 h, 97–99% (ii) 1.5–2 eq. $\text{HSiCl}_n\text{Me}_{(3-n)}$, Et_2O , Karstedt's catalyst, rt., 24 h, 96–99%.

Table 1Selected NMR chemical shifts [ppm] of compounds 3, 4 and 5 in $CDCl_3$ (298 K)

Compound	п	$SiCl_nMe_{(3-n)}$	Ph ₂ Si	Ph ₂ SiCH=	=CHSiCl _n Me _(3-n)
3 (SiClMe ₂)	1	16.7	-24.7	7.12	6.72
4 (SiCl ₂ Me)	2	14.1	-21.1	7.33	6.69
$5(SiCl_3)$	3	-6.1	-20.6	7.49	6.65

Table 2 Selected NMR chemical shifts [ppm] of compounds 6, 7 and 8 in CDCl₃ (298 K)

Compound	п	$SiCl_nMe_{(3-n)}$	Ph ₂ Si	Ph_2SiCH_2	$CH_2SiCl_nMe_{(3-n)}$
6 (SiClMe ₂)	1	33.0	-3.6	1.12	0.74
7 (SiCl ₂ Me)	2	33.3	-3.6	1.23	1.02
8 (SiCl ₃)	3	12.9	-3.4	1.29	1.29

cleavage of one of the two side arms. Owing to silicon carbide formation elemental analyses of these compounds gave misleading results.

Single crystals suitable for X-ray diffraction experiments of 3 (see ESI, Fig. S1[†]) and 5 were obtained by slow evaporation of concentrated dichloromethane solutions. Due to similarity of the molecular geometry, only chlorosilane 5 is presented in Fig. 2.

Bis(trichlorosilylvinyl)diphenylsilane (5) crystallizes in the monoclinic space group C2/c, with four molecules in the unit cell. The molecule is located on a two-fold axis. The C==C double bond C(1)–C(2) [1.330(5) Å] is of nearly the same length

Fig. 2 Molecular structure of **5** in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms of the phenyl substituents are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl(1)–Si(2) 2.039(2), Cl(2)–Si(2) 2.009(2), Cl(3)–Si(2) 2.023(2), Si(1)–C(1) 1.864(4), Si(1)–C(3) 1.872(4), Si(2)–C(2) 1.821(4), C(1)–C(2) 1.330(5); C(1)–Si(1)–C(1') 110.1(3), C(3)–Si(1)–C(1') 107.2(2), C(3)–Si(1)–C(3') 110.1(2), C(2)–C(1)–Si(1) 125.1(3), C(1)–C(2)–Si(2) 123.3(3), C(2)–Si(2)–Cl(1) 110.7(1), Cl(1)–Si(2)–Cl(2) 108.0(1), Cl(1)–Si(2)–Cl(3) 107.8(1), Cl(2)–Si(2)–Cl(3) 107.2(1). Symmetry equivalent atoms are generated by the operation 1 - x, y, 1/2 - z.

as observed in other hydrosilylated products.^{2,22} Both C=C–Si angles $[C(2)-C(1)-Si(1) \ 125.1(3)^{\circ}$ and $C(1)-C(2)-Si(2) \ 123.3(3)^{\circ}]$ are wide. The torsion angle $Si(1)-C(1)-C(2)-Si(2) \ [171.3(2)^{\circ}]$ is slightly smaller than the expected 180° . Si(2) is tetrahedrally coordinated. Deviations from ideal tetrahedral angle are as predicted by the VSEPR model: smaller for the Cl–Si–Cl angles and wider for the C–Si–Cl angles.^{23,24}

Fluorination reactions

To increase the Lewis acidity, the bidentate molecules **3–8** were converted into fluorosilanes by applying an excess of antimony trifluoride.²⁵ In the course of these reactions we frequently faced the occurrence of antimony trichloride contents in our products which were difficult to identify by the usual spectroscopic methods. We assume the formation of SbCl₃arene complexes to be the case.²⁶ Remaining traces of antimony trichloride (less than 10% of the isolated yields) were removed by sublimation (10^{-2} mbar, 40 °C) and the absence of SbCl₃ was proven by the Carr–Price test.²⁷ The fluorosilanes **9**, **10**, **12** and **13** were obtained nearly quantitatively as colorless highly viscous oils. Trifluoro compounds **11** and **14** were isolated by sublimation (10^{-2} mbar, 80 °C) as colorless crystals in yields slightly below 90% (Scheme 3).

Selected ¹H, ¹⁹F and ²⁹Si NMR chemical shifts and coupling constants of the unsaturated fluorosilanes 9, 10 and 11 in CDCl₃ at ambient temperature are listed in Table 3. The multiplicities of the vinylic proton signals in the ¹H NMR spectra [9 (dd), 10 (dt) and 11 (dq)] are characteristic for the substitution pattern at the terminal silicon atoms. The vinylic coupling (~23 Hz) in 9-11 again proves the trans-substitution pattern at the C=C double bonds. Along the series of compounds 9 to **11**, *i.e.* upon increasing the number of fluorine atoms, the ²⁹Si NMR chemical shifts of the fluorosilyl groups are shifted to higher field. The ¹⁹F resonances are split due to coupling to the methyl and vinyl protons adjacent to the fluorosilyl group; this results in a doublet of septets for 9, a doublet of quartets for 10 and a doublet for 11, respectively. Single crystals suitable for X-ray diffraction of 11 were obtained by slow evaporation of a concentrated solution in diethyl ether (Fig. 3).



Scheme 3 Syntheses of 9-14 via chlorinated species 3-8. Reagents and conditions: (i) SbF₃, pentane, rt., 20 h, 86–100%.

Bis(trifluorosilylvinyl)diphenylsilane (11) crystallizes in the monoclinic space group $P2_1/c$, with four molecules per unit cell. Both trifluorosilyl groups are disordered at two positions. The C=C double bonds C(1)–C(2) and C(3)–C(4) exhibit equal lengths within experimental error and both are shorter than typical silyl-substituted C=C double bonds.²⁸ The electron-withdrawing effect of the trifluorosilyl group leads to short bonds for C(2)–Si(2) [1.820(2) Å] and C(4)–Si(3) [1.824 (3) Å]. The olefinic angles are widened [from C(3)–C(4)–Si(3) 121.6(2)° to Si(1)–C(1)–C(2) 125.3(2)°] and the coordination spheres about the C=C double bonds deviate slightly from planarity as is indicated by the torsion angles Si(1)–C(1)–C(2)–Si(2) at 172.8(1)° and Si(1)–C(3)–C(4)–Si(3) at 177.4(1)°.

EI mass spectroscopy of the flexible bidentate molecules **12**, **13** and **14** resulted in the same fragmentation of one side arm as was observed for the corresponding chlorosilanes; molecular ions could therefore not be detected. Elemental analyses failed to give reliable results owing to the high fluorine and silicon content. Selected ¹H, ¹⁹F and ²⁹Si NMR chemical shifts of the saturated fluorosilanes **12**, **13** and **14** in CDCl₃ are listed in Table 4.

The ¹⁹F NMR spectra reveal diagnostic patterns for the coupling between the methylene protons and the fluorine atoms at the adjacent fluorosilyl group. This results in a triplet for **14**. The coupling with the methyl groups of **12** and **13**



Fig. 3 Molecular structure of **11** in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. For clarity, minor occupied disordered atoms and hydrogen atoms of the phenyl substituents are omitted. Selected bond lengths [Å] and angles [°]: Si(1)-C(1) 1.877(2), Si(1)-C(3) 1.875(2), Si(1)-C(5) 1.868(2), C(1)-C(2) 1.326(3), C(3)-C(4) 1.337(3), C(2)-Si(2) 1.820(2), Si(2)-F(1) 1.544(3), Si(2)-F(2) 1.602(2), Si(2)-F(3) 1.548(2); C(3)-Si(1)-C(1) 107.6(1), C(5)-Si(1)-C(1) 109.1(1), C(5)-Si(1)-C(3) 110.8(1), C(11)-Si(1)-C(1) 107.3(1), C(2)-C(1)-Si(1) 125.3(1), C(1)-C(2)-Si(2) 122.9(1), F(1)-Si(2)-C(2) 111.1(1), F(1)-Si(2)-F(3) 111.0(2), F(1)-Si(2)-F(2) 106.5(2), F(2)-Si(2)-F(3) 103.0(2).

entails higher order which could not be better resolved, even at 470 MHz. The ${}^{1}J_{\text{Si,F}}$ coupling constants – extracted from the 29 Si NMR spectra – confirm the assumed coupling patterns [12 280.1 Hz (d), 13 299.0 Hz (t) and 14 286.0 (q)]. Single crystals suitable for X-ray diffraction of 14 were obtained by sublimation (10^{-2} mbar, 80 °C) (Fig. 4).

Bis(trifluorosilylethyl)diphenylsilane (14) crystallizes in the monoclinic space group $P2_1/n$, with four molecules per unit cell. The angle between the two side arms at the central silicon atom is widened to $112.1(1)^{\circ}$ [C(3)–Si(1)–C(1)]. As expected the Si–C single bonds between the methylene carbon atoms and the silicon atoms are shorter at the Lewis acidic fluorosilyl groups [C(2)–Si(2) 1.827(2) and C(4)–Si(3) 1.816(2) Å] than towards the central silicon atom [Si(1)–C(1) 1.876(2) and Si(1)–C(3) 1.876(2) Å]. The C–C single bonds fall within the normal range for ethylene bridges between silyl groups [C(1)–C(2) 1.548(2) and C(3)–C(4) 1.551(2) Å].²⁹ All Si–F bond lengths are in a range from 1.555(2) Å [Si(3)–F(6)] to 1.577(1) Å [Si(2)–F(1)], the F–Si–F angles are all smaller than the typical tetrahedral angle [from F(6)–Si(3)–F(4) 105.0(1)° to F(2)–Si(2)–F(3) 106.8(1)°].

Table 3 Selected NMR shifts [ppm] and coupling constants [Hz] of compounds 9, 10 and 11 in CDCl₃ (298 K)

Compound	п	$SiF_nMe_{(3-n)}$	=CHSiF _n Me _(3-n)	³ <i>J</i> н,н; ³ <i>J</i> ғ,н	$\mathrm{Si}F_n\mathrm{Me}_{(3-n)}$
9 (SiFMe ₂)	1	17.7	6.71 (dd)	22.8; 2.8	-162.1
10 (SiF ₂ Me)	2	-16.1	6.54 (dt)	23.0; 2.4	-137.1
11 (SiF ₃)	3	-78.1	6.39 (dq)	23.1; 3.4	-141.5

Table 4	Selected NMR shifts	[ppm] of compounds	12, 13,	and 14 in	CDCl ₃ (2	298 K)
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Compound	п	$SiF_nMe_{(3-n)}$	Ph_2SiCH_2	$CH_2SiF_nMe_{(3-n)}$	$\mathrm{Si}F_n\mathrm{Me}_{(3-n)}$	
12 (SiFMe ₂)	1	33.1	1.13	0.65	-163.0	
13 (SiF_2Me)	2	2.4	1.14	0.69	-137.5	
$14(SiF_3)$	3	-59.8	1.23	0.88	-139.6	





Fig. 4 Molecular structure of 14 in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms of the phenyl substituents are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)–C(1) 1.876(2), Si(1)–C(3) 1.876(2), Si(1)–C(5) 1.877(2), Si(1)–C(11) 1.880(2), C(1)–C(2) 1.548(2), C(3)–C(4) 1.551(2), C(2)–Si(2) 1.827(2), C(4)–Si(3) 1.816(2), Si(2)–F(1) 1.577(2), Si(2)–F(2) 1.570(1), Si(2)–F(3) 1.570(1); C(3)–Si(1)–C(1) 112.1(1), C(5)–Si(1)–C(1) 107.8(1), C(5)–Si(1)–C(3) 111.5(1), C(11)–Si(1)–C(1) 109.5(1), C(2)–C(2)–Si(2) 112.2(1), F(1)–Si(2)–C(2) 111.5(1), F(1)–Si(2)–F(3) 105.2(1), F(1)–Si(2)–F(2) 105.5(1), F(2)–Si(2)–F(3) 106.8(1).

Fluoride complexation supported by 18-crown-6

The behavior of the bidentate Lewis acids 9-14 towards fluoride ions was analyzed in complexation reactions on NMR tube scale.^{10,14} Primarily, we tested the conditions described by Pietschnig using potassium fluoride acetone.30 in Interestingly, we did not observe a reaction with our most Lewis acidic compounds 11 or 14. Even after refluxing for several days, no changes, neither in the ¹H nor in the ¹⁹F NMR spectra, were detected. To minimize the interaction between potassium and fluoride ions as well as to increase the reactivity and solubility we added 18-crown-6.1,31 Despite many reports on benzene, toluene or THF³² as suitable solvents for this reaction, in our hands [K·18-crown-6]⁺F⁻ could only be generated using dichloromethane and spray-dried potassium fluoride.^{7,28a,31c,33}

First we attempted the reaction of 9-14 with two equivalents of isolated $[K\cdot18\text{-}crown-6]^+F^-$ in chloroform- d_1 to establish a ratio of 1:1 of fluoride ions and Lewis-acidic silyl groups. The less Lewis-acidic bidentate molecules 9 and 12 bearing dimethylfluorosilyl groups showed no reaction

towards $[K\cdot18$ -crown-6]⁺F⁻. The bidentate compounds **10** and **13** with difluoromethylsilyl groups result in an uninterpretable product mixture in the ¹H NMR and ¹⁹F NMR spectra, only the most Lewis acidic trifluorosilyl compounds **11** and **14** forms one complexation product as exemplarily shown for the unsaturated trifluorosilyl bidentate molecule **11** (Fig. 5).

An equimolar amount of $[K\cdot18\text{-}\mathrm{crown-6}]^+\mathrm{F}^-$ was added to **11** and the reaction was followed by ¹H, ¹⁹F and ²⁹Si NMR spectroscopy. Compared to the spectrum of **11**, the ¹H NMR spectrum of product **15** (1 eq. $[K\cdot18\text{-}\mathrm{crown-6}]^+\mathrm{F}^-$ added) displays a slight downfield shift and disappearance of the multiplicity for the resonance (6.48 ppm) of the CH group adjacent to the silicate unit. The fact that both side arms are chemically equivalent on the NMR timescale and that all olefinic proton signals of product **15** are broadened and shifted $[\delta (^1\text{H}) = 7.67$ to 7.57 ppm and 6.39 to 6.48 ppm], indicates rapid exchange of fluoride ions and involvement of both trifluorosilyl groups in fluoride binding.

Addition of a second equivalent of $[K\cdot18\text{-crown-6}]^+F^-$ leads to formation of the bissilicate **16**. The even broader lines of the olefinic protons (Fig. 5) for **16** (compared to **15** and **11**) indicate an accelerated fluoride exchange (it cannot be distinguished, whether it is intra- or intermolecular or a positional exchange within one SiF₄ group by pseudorotation). Even the hydrogen atoms of the phenyl groups are influenced by the formation of monosilicate **15** and bisilicate **16**. Selected ¹H, ¹⁹F and ²⁹Si NMR chemical shifts of the unsaturated compounds **11**, **15** and **16** are listed in Table 5.



Fig. 5 ¹H NMR (500 MHz) spectra of the Lewis-acidic bidentate molecule **11** and its conversion with one (\rightarrow **15**) and two equivalents (\rightarrow **16**) of [K·18-crown-6]⁺F⁻ in chloroform- d_1^* at 298 K.

Compound	SiF	SiF	o-ArH	=CHSiF
11 (SiF ₃)	-78.1	-141.5 (d)	7.47	6.39 (dq)
15 (monosilicate)	n.o.	-124.0 (br)	7.52	6.48 (d)
16 (bissilicate)	-129.6	-121.5 (br)	7.56	6.62 (d)

Neither by ²⁹Si nor by ¹H,²⁹Si HMBC NMR experiments the ²⁹Si chemical shifts of monosilicate **15** were observable at ambient temperature, except that of the central silicon atom ($\delta = -21.4 \text{ ppm}$). After adding a second equivalent of F⁻, we detected a signal at -129.6 ppm, a typical range for pentacoordinated silicates.^{30,33,34} We conclude that a bissilicate **16** with two anionic tetrafluorosilicate groups was formed. Its ¹⁹F NMR spectrum shows a sharp singlet at -121.5 ppm for these groups (Fig. 6). The chemical equivalence of all fluorine atoms at ambient temperature on the NMR timescale implies rapidly exchanging axial and equatorial fluorine atoms.

The ¹⁹F NMR spectrum of **15**, the monosilicate, displays a broad signal at -124.0 ppm, *i.e.* a chemical shift between the signals of **11** (with two SiF₃ groups) and **16** (with two SiF₄⁻ groups). This signifies a fluoride ion exchange process between SiF₃- and SiF₄ groups in **15**. Consequently, we performed low-temperature ¹⁹F NMR measurements on silicate **15** in order to determine the position of the added fluoride ion in

11 at 298 K Ph₂S SiF 3 15 at 298 K 15 at 178 K Ph₂S 4.00-T 3.26 16 at 298 K Ph₂S SiF -100 -110 -120 -130-140 -150δ [ppm]

Fig. 6 ¹⁹F NMR spectra of **11**, **15** (1 eq. [K·18-crown-6]⁺F⁻ added) and **16** (2 eq. [K·18-crown-6]⁺F⁻ added) at various temperatures in dichloromethane-d₂ (564 MHz); # denotes impurity (*ca.* 1% at rt.).

solution (Fig. 6).^{5,7} At 178 K one observes two signals at -121 and -141 ppm, typical for tetra- and pentacoordinated silicon species.³⁴ This does not provide evidence for a bridging fluoride ion between the two side arms, but rather for the simultaneous presence of SiF₃ and SiF₄⁻ groups. The intensity ratio of 4:3 underpins this interpretation.

Further proof stems from a structure determination in the solid state. Single crystals suitable for X-ray diffraction experiments of **15** were obtained by slow evaporation of a dichloromethane solution and show the presence of two differently coordinated fluorosilyl groups (Fig. 7).

The potassium 18-crown-6 salt of silicate 15 crystallizes in the monoclinic space group $P2_1$ with two molecules in the unit cell. To our knowledge, this is the first structurally characterized potassium 18-crown-6 silicate polymer. The potassium atom is located 0.642(2) Å towards the trigonal-bipyramidal coordinated silicon atom above the mean plane defined by the six oxygen atoms of the 18-crown-6 ligand, the K…O contacts ranging from 2.814(3) Å to 2.937(3) Å. Four K…F contacts can be obtained: three of them to fluorine atoms of the trigonalbipyramide, one short contact to the axial fluorine atom (F(1))...K(1) 2.682(3) Å) and two longer ones to the equatorial fluorine atoms [K(1)...F(2) 3.155(4) Å and K(1)...F(3) 3.128(3) Å]. The fourth potassium-fluorine contact is built to one fluorine atom of the trifluorosilyl group, which is disordered in ratio 81:19. The major occupied position of the fluorine atom is located 2.65(1) Å from K1. This contact assembles the polymeric structure by translation of the molecule along 101. All Si(3)-F bonds are of equal length within experimental error



Fig. 7 Molecular structure of **15** in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Only vinyl hydrogen and major occupied disordered atoms are shown for clarity. Selected bond lengths [Å] and angles [°]: K(1)-F(1) 2.682(3), K(1)-F(2) 3.155(4), K(1)-F(3) 3.128(3), K(1)-F(7) 2.86(3), Si(2)-F(1) 1.695(3), Si(2)-F(2) 1.609(3), Si(2)-F(3) 1.622(3), Si(2)-F(4) 1.663(3), Si(2)-C(2) 1.877(5), Si(3)-F(5) 1.48(3), Si(3)-F(6) 1.41(3), Si(3)-F(7) 1.45(3), Si(3)-C(4) 1.828(5), C(1)-C(2) 1.343(7), C(3)-C(4) 1.324(7), Si(1)-C(1) 1.862(4), Si(1)-C(3) 1.879(5), Si(1)-C(5) 1.860(5), Si(1)-C(11) 1.868(5); F(1)-K(1)-F(7) 169.0(8), Si(2)-F(1)-K(1) 103.6(1), Si(3)-F(7)-K(1) 149(2), F(1)-Si(2)-F(4) 177.2(2), F(1)-Si(2)-F(3) 123.6(2), C(2)-Si(2)-F(3) 123.9(2), F(2)-Si(2)-F(3) 112.3(2), C(4)-Si(3)-F(7) 111.0(1), F(5)-Si(3)-F(7) 108.6(2), C(1)-C(3) 107.8(2). Symmetry equivalent atoms are generated by the operations -1 + x, y, 1 + z.

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and shorter than the Si-F bond in 11. As expected for trigonalbipyramidally coordinated silicates, the Si-F_(ax) bonds are found to be remarkably longer than the Si-F_(eq) bonds [e.g. Si(2)–F(1) 1.695(3) Å vs. Si(2)–F(2) 1.609(3) Å].³⁵ The axial fluorine atoms are nearly in plane with the C=C double bond C(1)-C(2) as is indicated by the torsion angles C(1)-C(2)-Si(2)-F(4) $[6.2(5)^{\circ}]$ and C(1)-C(2)-Si(2)-F(1) $[173.3(4)^{\circ}]$ and the hydrogen fluorine contacts $H(1)\cdots F(4)$ (2.330(3) Å) and $H(2)\cdots F(1)$ (2.468(3) Å). The angles at the pentacoordinated silicon center are slightly distorted towards the potassium atom as indicated by the angles F(1)-Si(2)-F(3) 88.0(2)°, F(1)-Si(2)-F(2) 88.1(2)° and F(2)-Si(2)-F(3) 112.3(2)°.^{31c} The crystal structure of 15 is in a good agreement with our low temperature NMR studies in solution. Two differrently coordinated silicon atoms are formed: one tetracoordinated silicon and one pentacoordinated silicate.

Due to the fact that we observed only one ¹⁹F NMR singlet for bissilicate **16**, although the axial and equatorial fluorine atoms of a pentacoordinated silicon species are not chemically equivalent, ^{7,30,36} low-temperature NMR investigations were performed. Even at 195 K no signal-splitting in the ¹⁹F NMR spectrum into $F_{(ax)}$ and $F_{(eq)}$ resonances was observed (likely due to pseudorotation of the SiF₄ group). In ¹H, ²⁹Si HMBC experiments of **16** a quintet-like signal at –130 ppm (¹*J*_{Si,F} = 205 Hz) can be observed at 203 K, confirming the formation of a bistetrafluorosilicate (Scheme 4).

Comparable results to those described above are found for the conversion of the saturated bidentate compound **14** with one equivalent of $[K\cdot18$ -crown-6]⁺F⁻ (see ESI⁺ for details). This



Scheme 4 Syntheses of the monosilicates 15 and 16 and the bissilicates 17 and 18, respectively. Reagents and conditions: (i) 1 eq. $[K\cdot18-crown-6]^+F^-$, CH₂Cl₂, rt., 2–3 h, quant. (ii) 2 eq. $[K\cdot18-crown-6]^+F^-$, CH₂Cl₂, rt., 2–4 h, quant.

gives rise to the assumption that the higher flexibility of **14** takes no influence towards the complexation of fluoride ions. Results of the low-temperature NMR measurements and the crystal structure show the formation of the corresponding potassium 18-crown-6 coordination polymer with a monosilicate anion, compound **17** (see ESI, Fig. S3†). Further addition of potassium fluoride and 18-crown-6 leads to the formation of a bissilicate analogous to **16**.

Fluoride complexation supported by [2.2.2]cryptand

In order to further decrease the observed interactions between potassium and fluoride ions [2.2.2]cryptand was used as a complexing agent for potassium.³⁷ Preparative access to $\{K\cdot[2.2.2]cryptand\}^+F^-$ could be realized by using spray-dried potassium fluoride and [2.2.2]cryptand in acetone. This was necessary, as an attempt to prepare the salt in dichloromethane led to formation of the chloride salt $\{K\cdot[2.2.2]cryptand\}^+Cl^-$, indicating the substitution of chloride in CH_2Cl_2 by this activated form of potassium fluoride.³⁸ Consequently, we had to use acetone as a solvent for the low-temperature investigations of fluoride complexation under with $\{K\cdot[2.2.2]cryptand\}^+F^-$.

The conversion of one and two equivalents of the {K·[2.2.2] cryptand}⁺F⁻ salt with the rigid and flexible fluorophilic bidentate molecules **11** and **14** led to the formation of monosilicates **19** and **21** as well as the corresponding bissilicates **20** and **22**. Selected ¹H, ¹⁹F and ²⁹Si NMR chemical shifts of the rigid bidentate molecules (**19**, **20**) and the more flexible ones (**21**, **22**) in acetone- d_6 at ambient temperature are listed in Table 6.

In contrast to the starting materials **11** and **14** the ¹H NMR spectra of monosilicates **19** and **21** show no ${}^{3}J_{F,H}$ coupling to the hydrogen atoms adjacent to the fluorosilyl group. This indicates rapid exchange of the fluoride ion between both Lewis acidic sites in solution. No ²⁹Si NMR resonances for **19** or **21** were observable at ambient temperature, except for the doubly phenyl substituted Si atoms. The ¹⁹F NMR spectra of both monosilicates **19** and **21** show broad signals at ambient temperature (-123.6 and -120.1 ppm, respectively). In order to analyze the complexation in solution, ¹⁹F NMR spectra at various temperatures were recorded for the conversion reactions of **11** with one or two equivalents of {K·[2.2.2] cryptand}⁺F⁻ (Fig. 8).

The ¹⁹F NMR spectrum of **11** displays a doublet at –141.5 ppm (${}^{3}J_{F,H} = 3.4 \text{ Hz}$). After conversion with two equivalents of {K·[2.2.2]cryptand}⁺F⁻ a sharp singlet of bissilicate **20**

Table 6 Selected NMR shifts [ppm] of the vinylic silicates **19** and **20** (x = 1) and the saturated silicates **21** and **22** (x = 2) in acetone- d_6 at 298 K (n.o. = not abservable)

Compound	SiF	SiF	CH _x SiF
19 (monosilicate) 20 (bissilicate) 21 (monosilicate)	n.o. -130.2 n.o.	-120.1 -119.8 -123.6	6.62 6.68 0.75
22 (bissilicate)	-113.6	-117.3	0.65



Fig. 8 ¹⁹F NMR spectra (564 MHz) of trifluorosilyl compound **11**, silicate **19** (1 eq. {K·[2.2.2]cryptand}⁺F⁻) and bissilicate **20** (2 eq. {K·[2.2.2] cryptand}⁺F⁻) at various temperatures in acetone- d_6 solution.

was detected at -119.8 ppm. Addition of just one equivalent of $\{K\cdot[2.2.2]$ cryptand $\}^+F^-$ results in the formation of the corresponding monosilicate 19. For this and at ambient temperature, the ¹⁹F NMR spectrum displays a broad signal at -120.1 ppm, a shift value close to that of bissilicate 20. There occurs, already at ambient temperature, a clear separation of the resonances of the SiF_3 (-138 ppm) and SiF_4 groups (-120 ppm). Subsequent lowering the temperature leads to a slight downfield shift of the SiF₄ signal (from -120.1 to -118.5 ppm) and an increasing intensity of the sharp SiF₃ singlet. The broadening of the SiF₄ signal might be explicable by the slower exchange of axial and equatorial fluorine atoms (pseudo rotation in the silicon coordination sphere) also at low temperature. 19F NMR spectra at various temperatures of the flexible Lewis acidic bidentate molecule 14 were also recorded for the conversion with one (formation of 21) or two equivalents (formation of 22) of the fluoride salt (Fig. 9).

The ¹⁹F NMR spectra of **14** and **22** display sharp signals for the two chemically identical SiF₃ groups (-139.6 ppm, t, ${}^{3}J_{F,H} =$ 2.8 Hz) and SiF₄ groups (-117.3 ppm, s). The complexation of just one equivalent {K·[2.2.2]cryptand}⁺F⁻ results in the formation of **21**. In contrast to the less flexible **19**, monosilcate **21** shows a broad signal at -123.6 ppm in the ¹⁹F NMR spectrum at ambient temperature, which reflects exchange of fluoride



Fig. 9 ¹⁹F NMR spectra (564 MHz) of trifluorosilyl compound 14, silicate 21 (1 eq. {K·[2.2.2]cryptand}⁺F⁻) and bissilicate 22 (2 eq. {K·[2.2.2] cryptand}⁺F⁻) at various temperatures in acetone- d_6 solution.

ions between the two terminal Lewis acidic groups. Subsequent lowering the temperature leads to a downfield shift of the broad signal from -123.6 ppm to -116.4 ppm and an increasing of the SiF₃ group signal at -138 ppm. Analogous to the monosilicate 19, a separation of the tetra- and pentacoordinated silicon resonances is observed at low temperatures. In contrast to the 18-crown-6 monosilicates 15 and 17 as well as the [2.2.2]cryptand monosilicate 19, 21 displays a broader signal for the SiF₄ group at low temperature. The present data do not allow distinguishing the several possible dynamic processes including intra- and intermolecular fluoride exchange, pseudorotation in the silicon coordination sphere and assistance of the potassium ion in these processes. Lower temperatures would be necessary for a better resolution, but the melting point of acetone sets a limit to such measurements.

The ¹⁹F NMR spectra at 298 K of bissilicates **20** and **22** show sharp singlets at -119.8 (**20**) and -117.3 (**22**) ppm indicating the presence of two chemically equivalent side arms with rapid exchange of all axial and equatorial fluorine atoms due to pseudo rotation. The ²⁹Si NMR spectra of bissilicates **20** and **22** (determined by ¹H, ²⁹Si HMBC experiments) display signals at -113.6 and -130.2 ppm, respectively, a typical range

for pentacoordinated silicon atoms.^{5,7} The solid state structures of **20** and **22** are compatible with the NMR data of the corresponding compounds. These molecular structures are the first structurally characterized bissilicates with two [2.2.2]cryptands bearing potassium cations (Fig. 10 and 11).

Potassium [2.2.2]cryptand bissilicate **20** crystallizes in the triclinic space group $P\overline{1}$ with two molecules per unit cell. The vinylic angles are wider than in a typical trigonal-planar coordination geometry [Si(2)–C(14)–C(13) 127.2(1)°, C(14)–C(13)–Si(1) 126.7(1)°, Si(1)–C(15)–C(16) 124.4(2)°, C(15)–C(16)–Si(3) 125.4(2)°]. The pentacoordinated silicon atom Si(2) has a trigonal bipyramidal coordination geometry with longer axial Si(2)–F_(ax) bonds [1.673(1) and 1.693(1) Å] and shorter Si(2)–F_(eq) bonds [1.616(1) and 1.622(1) Å].³⁵ The other pentacoordinated geometry at Si(3) is more distorted; Si(3)–F(8) [1.734(2) Å] is the longest Si–F bond although F(8) is in equatorial position. The angles F(5)–Si(3)–F(8) [84.7(1)°] and F(8)–Si(3)–F(6) [86.2(1)°] are both smaller than 90°.

Despite saturation of the vinylic group potassium [2.2.2] cryptand bissilicate **22** is isostructural to **20**. The tetrafluorosilyl group at Si(2) displays a typical pentacoordinated silicate with longer axial bonds [Si(2)–F(1) 1.699(1) and Si(2)–F(3) 1.679(1) Å] and shorter equatorial ones [Si(2)–F(2) 1.621(1) and Si(2)–F(4) 1.615(1) Å]. The other SiF₄ group is deformed, the equatorial bond Si(3)–F(8) [1.660(1) Å] is as long as the axial bond Si(3)–F(5) [1.659(1) Å] due to an intermolecular H…F contact. The angles between the fluorine atoms are hardly influenced by this deformation [F(5)–Si(3)–F(6) 173.0(1)° and



Fig. 10 Molecular structure of 20 in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Only vinylic hydrogen and major occupied disordered atoms are shown for clarity. Selected bond lengths [Å] and angles [°]: Si(2)-F(1) 1.693(1), Si(2)-F(2) 1.622(1), Si(2)-F(3) 1.673(1), Si(2)-F(4) 1.616(1), Si(3)-F(5) 1.691(3), Si(3)-F(6) 1.658(2), Si(3)-F(7) 1.496(2), Si(3)-F(8) 1.734(2), Si(2)-C(14) 1.889(2), Si(3)-C(16) 1.903(3), C(13)-C(14) 1.334(2), C(15)-C(16) 1.295(4), Si(1)-C(13) 1.860(1), Si(1)-C(15) 1.892(3), Si(1)-C(1) 1.928(5), Si(1)-C(7) 1.876(1); F(1)-Si(2)-F(2) 89.0(1), F(1)-Si(2)-F(4) 89.7(1), F(2)-Si(2)-F(4) 116.4(1), F(1)-Si(2)-F(3) 178.1(1), F(1)-Si(2)-C(14) 89.2(1), C(14)-Si(2)-F(3) 92.5(1), C(14)-Si(2)-F(2) 120.8(1), F(5)-Si(3)-F(7) 91.3(1), F(5)-Si(3)-F(8) 84.7(1), F(5)-Si(3)-F(6) 170.9(1), F(7)-Si(3)-F(8) 118.1(2), F(5)-Si(3)-C(16) 103.2(1), C(16)-Si(3)-F(7) 110.8(1), C(16)-Si(3)-F(8) 130.3(1), C(1)-Si(1)-C(7) 109.3(1), C(13)-Si(1)-C(15) 112.1(1), Si(1)-C(14) 126.7(1), C(13)-C(14)-Si(2)-C(14) 124.4(2), C(15)-C(16)-Si(3) 125.4(2).



Fig. 11 Molecular structure of 22 in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Solely methylene hydrogen atoms of the bissilicates are shown for clarity. Selected bond lengths [Å] and angles [°]: Si(2)–F(1) 1.699(1), Si(2)–F(2) 1.621(1), Si(2)–F(3) 1.679(1), Si(2)–F(4) 1.615(1), Si(3)–F(5) 1.659(1), Si(3)–F(6) 1.706(1), Si(3)–F(7) 1.614 (1), Si(3)–F(8) 1.660(1), Si(2)–C(14) 1.885(2), Si(3)–C(16) 1.875(1), C(13)–C(14) 1.539(2), C(15)–C(16) 1.538(2), Si(1)–C(13) 1.877(1), Si(1)–C(15) 1.872(1), Si(1)–C(1) 1.918(4), Si(1)–C(7) 1.881(1); F(1)–Si(2)–F(2) 88.7(1), F(1)–Si(2)–F(4) 89.4(1), F(2)–Si(2)–F(4) 116.9 (1), F(1)–Si(2)–F(3) 176.9(1), F(1)–Si(2)–C(14) 89.3(1), C(14)–Si(2)–F(3) 93.7(1), C(14)–Si(2)–F(2) 120.1(1), F(5)–Si(3)–F(7) 89.4(1), F(5)–Si(3)–F(8) 88.3(1), F(5)–Si(3)–F(6) 173.0(1), F(7)–Si(3)–F(8) 118.6(1), F(5)–Si(3)–C(16) 90.6(1), C(16)–Si(3)–F(7) 123.6(1), C(16)–Si(3)–F(8) 117.8(1), C(1)–Si(1)–C(7) 108.5(1), C(13)–Si(1)–C(15) 108.6(1), Si(1)–C(13)–C(14) 117.7(1), C(13)–C(14)–Si(2) 121.0(1), Si(1)–C(15)–C(16) 116.9(1), C(15)–C(16)–Si(3) 117.8(1).



 $\label{eq:scheme 5} \begin{array}{l} \mbox{Syntheses of monosilicates 19, 21 and bissilicates 20, 22.} \\ \mbox{Reagents and conditions: (i) 1 eq. } \{K\cdot[2.2.2]\mbox{cryptand}\}^+F^-, \mbox{ acetone, rt., } 30 min, \mbox{ quant. (ii) 2 eq. } \{K\cdot[2.2.2]\mbox{cryptand}\}^+F^-, \mbox{ acetone, rt., } 30 min, \mbox{ quant. } \end{array}$

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F(7)-Si(3)-F(8) 118.6(1)°]. Both side arms are found to be almost in *anti*-conformation, as the corresponding Si(1)–C–C–Si torsion angles are close to 180°. The C–Si(1)–C angles are at least 108.5° indicating a tetrahedral geometry at Si(1). Due to the torsion angle C(13)–Si(1)–C(15)–C(16) [55.3(1)°] the two silicate groups are not positioned at maximum distance to each other.

Scheme 5 summarizes the reactions taking place, when the Lewis acidic bidentate molecules are converted with one or two equivalents of $\{K\cdot[2.2.2]cryptand\}^+F^-$. Both reaction pathways have been elucidated by low temperature NMR studies and X-ray crystallographic structure determinations.

Conclusion

Starting from diethynyldiphenylsilane (1) and divinyldiphenylsilane (2), six new (methyl)chlorosilanes (3–8) have been synthesized by hydrosilylation reactions in excellent yields (>95%). These chlorosilanes were converted into the corresponding fluorosilanes (9–14). These new bidentate molecules exhibit a variety of Lewis acidities and all bear two equivalent fluorosilyl groups. The latter are connected by two types of backbones with different flexibility.

Quantitative complexation of the fluoride guest ion towards the corresponding mono- and bissilicates is observed by reacting the bis(trifluorosilyl) hosts **11** and **14** with one or two equivalents of $[K\cdot18\text{-}crown-6]^+F^-$ or $\{K\cdot[2.2.2]cryptand\}^+F^-$. Low-temperature NMR and X-ray diffraction experiments indicate in all cases the occurrence of monosilicates and bissilicates in solution and in the solid state depending on the amount of fluoride added.

The complexation of one equivalent fluoride guest results in a fluoride ion exchange process between SiF_{3} - and SiF_{4} groups for the monosilicates **15**, **17**, **19** and **21**. For the solution phase low-temperature NMR spectroscopy does not provide evidence for a bridging fluoride ion between the two side arms, but rather for the simultaneous presence of SiF_{3} and SiF_{4}^{-} groups. This is in line with the crystallographic results for the solid state: molecules **15** and **17** contain both, SiF_{3} and SiF_{4}^{-} groups, and form potassium-bridged polymeric chains. Bissilicates **16**, **18**, **20** and **22** have been quantitatively obtained by complexation of two equivalents fluoride guest. All SiF_{4} groups show a rapid pseudorotation in the silicon coordination sphere between axial and equatorial fluorine atoms even at low temperature.

Experimental

Materials and methods

NMR spectra were recorded on a Bruker DRX 500 and a Bruker Avance III 500 instrument. The chemical shifts (δ) were measured in ppm with respect to the solvent (CDCl₃: ¹H NMR δ = 7.26 ppm, ¹³C NMR δ = 77.16 ppm) or referenced externally (²⁹Si: SiMe₄; ¹⁹F: CFCl₃). EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by push rod in aluminum crucibles. Ions were accelerated by 8 kV. The reactions were carried out by using freshly distilled and dry solvents from solvent stills (acetone was isopropanol-free and dried over anhydrous 4A molecular sieves and then distilled). Potassium fluoride (spray dried quality), 18-crown-6 and [2.2.2]cryptand were all dried in vacuum at about 200 °C before use. Elemental analyses were performed with CHNS elemental analyzer HEKAtech EURO EA (too low values for carbon are due to the known formation of silicon carbide and potassium carbonate).

Synthetic procedures

Diethynyldiphenylsilane (1). Ethynyl magnesium bromide solution (0.50 M in THF; 50 mL, 25 mmol) was diluted in dry THF (30 mL). Freshly distilled diphenyl dichlorosilane (2.5 mL, 12 mmol) was added dropwise at 0 °C. After the pale orange solution was stirred overnight at ambient temperature, it was heated to reflux for 1 h. The reaction was quenched with sat. aq. ammonium chloride solution (50 mL), and the phases were separated. All volatile compounds of the organic phase were removed and the crude product was subjected to a shortpath distillation at 120 °C at 10⁻² mbar. The substance is yielded in the pure state as colorless crystals. Yield: 2.52 g (91%). ¹H NMR (300 MHz, CDCl₃): δ = 7.77 (m, 4H, *o*-*H*), 7.44 (m, 6H, *m*-/*p*-H), 2.75 (s, 2H, C \equiv CH) ppm. ¹³C{¹H} NMR $(75 \text{ MHz}, \text{CDCl}_3): \delta = 134.9 (o-C), 131.4 (i-C), 130.8 (p-C), 128.4$ (*m*-*C*), 97.5 (C≡*C*H), 83.5 (*C*≡*C*H) ppm. ²⁹Si{¹H} NMR (60 MHz, CDCl₃): $\delta = -48.3$ ppm. Elemental analysis calcd (%) for C₁₆H₁₂Si (*M*_r = 232.35): C 82.71, H 5.21; found: C 82.90, H 5.64. EI-MS (70 eV): m/z [assignments] = 231.1, 206.1, 178.1, 155.0, 129.0, 103.0, 77.0. HRMS (EI, 70 eV): calculated for C₁₆H₁₂Si⁺: 232.07028; measured: 232.06996; dev. [ppm]: 0.32, dev. [mmu]: 1.38.

Divinyldiphenylsilane (2). Vinylmagnesium chloride solution (1.9 M in THF; 20 mL, 38 mmol) was diluted in dry THF (60 mL). Freshly distilled diphenyldichlorosilane (3.2 mL, 15 mmol) was added dropwise at 0 °C. After the brown solution was stirred overnight at ambient temperature, it was heated to reflux for 1 h. The reaction was quenched with sat. aq. ammonium chloride solution (40 mL), and the phases were separated. All volatile compounds of the organic phase were removed under reduced pressure and the oily crude product was distilled at 80 °C at 10⁻² mbar to give a colorless liquid. Yield: 3.26 g (92%). ¹H NMR (500 MHz, $CDCl_3$): δ = 7.56 (m, 4H, *o*-*H*), 7.40 (m, 6H, *m*-/*p*-*H*), 6.52 (dd, ³*J*_{H,H} = 20.3 Hz, ${}^{3}J_{H,H}$ = 14.6 Hz, 2H, SiCH=CH₂), 6.28 (dd, ${}^{3}J_{H,H}$ = 14.6 Hz, ${}^{2}J_{\rm H,H}$ = 3.7 Hz, 2H, *trans-H*), 5.83 (dd, ${}^{3}J_{\rm H,H}$ = 20.3 Hz, ${}^{2}J_{\rm H,H}$ = 3.7 Hz, 2H, *cis*-H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 136.6 (CH=CH₂), 135.7 (o-C), 134.4 (i-C), 134.0 (CH=CH₂), 129.6 (*p-C*), 128.0 (*m-C*) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): $\delta = -20.7$ ppm. EI-MS (70 eV): m/z [assignments] = 236.1, 209.1, 183.1, 158.1, 132.0, 105.0, 79.0. HRMS (EI, 70 eV): calculated for $C_{16}H_{16}Si^+$: 236.10158; measured: 236.10082; dev. [ppm]: 3.22, dev. [mmu]: 0.76.

General procedure for hydrosilylation

Diethynyldiphenylsilane (1) was dissolved in the corresponding chlorosilane. Karstedt's catalyst (1% (wt) Pt in toluene, 1–3 drops) was added *via* a syringe and the pale yellow reaction mixture was stirred for 2 h at ambient temperature. Remaining chlorosilane was removed *in vacuo* and the product was obtained analytically pure.

Divinyldiphenylsilane (2) was dissolved in Et₂O (2–4 mL). Chlorosilane (2.5–4 eq.) and Karstedt's catalyst (1% (wt) Pt in toluene, 1–3 drops) was added *via* a syringe and the reaction mixture was stirred for 3 d at ambient temperature. All volatile compounds were removed under reduced pressure and the product was obtained analytically pure.

Bis(chlorodimethylsilylvinyl)diphenylsilane (3). Yield: 704 mg (97%). ¹H NMR (500 MHz, CDCl₃): δ = 7.43 (m, 10H, Ph-*H*), 7.12 (d, ³*J*_{H,H} = 22.4 Hz, 2H, Ph₂SiC*H*), 6.72 (d, ³*J*_{H,H} = 22.4 Hz, 2H, CHSiClMe₂), 0.52 (s, 12H, CH₃) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 152.1 (Ph₂SiCH), 147.3 (CHSiClMe₂), 135.8 (*o*-*C*), 133.2 (*i*-*C*), 130.0 (*p*-*C*), 128.2 (*m*-*C*), 1.8 (*C*H₃) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 16.7 (*Si*ClMe₂), -24.7 (Ph₂S*i*) ppm. EI-MS (70 eV): *m*/*z* [assignments] = 420.1, 405.1, 376.1, 327.1, 250.0, 217.0, 183.1, 135.1, 105.0, 93.0. HRMS (EI, 70 eV): calculated for C₂₀H₂₆Cl₂Si₃⁺: 420.07139; measured: 420.07194; dev. [ppm]: 1.31, dev. [mmu]: 0.55.

Bis(dichloromethylsilylvinyl)diphenylsilane (4). Yield: 1.51 g (99%). ¹H NMR (500 MHz, CDCl₃): δ = 7.47 (m, 10H, Ph-*H*), 7.33 (d, ³*J*_{H,H} = 22.2 Hz, 2H, Ph₂SiC*H*), 6.69 (d, ³*J*_{H,H} = 22.2 Hz, 2H, CHSiCl₂Me), 0.90 (s, 6H, CH₃) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 150.2 (Ph₂SiCH), 148.2 (CHSiCl₂Me), 135.8 (*o*-*C*), 131.7 (i-*C*), 130.5 (*p*-*C*), 128.5 (*m*-*C*), 5.2 (CH₃) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 14.1 (*Si*Cl₂Me), -21.1 (Ph₂*Si*) ppm. EI-MS (70 eV): *m*/*z* [assignments] = 460.0, 381.9, 347.1, 270.0, 217.0, 183.1, 145.1, 105.0. HRMS (EI, 70 eV): calculated for C₁₈H₂₀Cl₄Si₃⁺: 459.96214; measured: 459.96331; dev. [ppm]: 2.54, dev. [mmu]: 1.17.

Bis(trichlorosilylvinyl)diphenylsilane (5). Yield: 1.18 g (98%). ¹H NMR (500 MHz, CDCl₃): δ = 7.49 (d, ³*J*_{H,H} = 21.9 Hz, 2H, Ph₂SiC*H*), 7.48 (m, 10H, Ph-*H*), 6.65 (d, ³*J*_{H,H} = 21.9 Hz, 2H, CHSiCl₃) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 152.7 (Ph₂SiC*H*), 145.1 (CHSiCl₃), 135.8 (*o*-*C*), 130.9 (*p*-*C*), 130.5 (*i*-*C*), 128.7 (*m*-*C*) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -6.1 (*SiCl*₃), -20.6 (Ph₂*Si*) ppm. EI-MS (70 eV): *m*/*z* [assignments] = 499.9, 423.8, 369.0, 326.9, 288.9, 243.1, 217.0, 183.1, 165.0, 131.1, 105.0. HRMS (EI, 70 eV): calculated for C₁₆H₁₄Cl₆Si₃⁺: 499.85290; measured: 499.85240; dev. [ppm]: 1.00, dev. [mmu]: 0.50.

Bis(chlorodimethylsilylethyl)diphenylsilane (6). Yield: 912 mg (96%). ¹H NMR (500 MHz, CDCl₃): δ = 7.50 (m, 4H, Ph-*H*), 7.38 (m, 6H, Ph-*H*), 1.12 (m, 4H, Ph₂SiCH₂), 0.74 (m, 4H, CH₂SiClMe₂), 0.39 (s, 12H, CH₃) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 135.3 (i-*C*), 135.1 (*o*-*C*), 129.6 (*p*-*C*), 128.1 (*m*-*C*), 11.4 (CH₂SiClMe₂), 3.6 (Ph₂SiCH₂), 1.1 (CH₃) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 33.0 (*Si*ClMe₂), -3.6 (Ph₂*Si*)ppm. EI-MS (70 eV): *m*/*z* [assignments] = 410.4, 303.3 [M - (CH₂CH₂SiClMe₂)]⁺, 260.9, 231.2, 250.0, 191.2, 149.1, 137.1, 123.1, 36.0.

Bis(dichloromethylsilylethyl)diphenylsilane (7). Yield: 654 mg (98%). ¹H NMR (500 MHz, CDCl₃): δ = 7.51 (m, 4H, Ph-*H*), 7.42 (m, 6H, Ph-*H*), 1.23 (m, 4H, Ph₂SiCH₂), 1.02 (m, 4H, CH₂SiCl₂Me), 0.76 (s, 6H, CH₃) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 135.1 (*o*-*C*), 134.1 (i-*C*), 129.9 (*p*-*C*), 128.3 (*m*-*C*), 14.4 (CH₂SiCl₂Me), 4.6 (Ph₂SiCH₂), 3.4 (CH₃) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 33.3 (*Si*Cl₂Me), -3.4 (Ph₂Si) ppm. EI-MS (70 eV): *m*/*z* [assignments] = 466.0, 323.0 [M - (CH₂CH₂SiCl₂Me)]⁺, 217.0, 183.1, 121.0, 105.0.

Bis(trichlorosilylethyl)diphenylsilane (8). Yield: 400 mg (99%). ¹H NMR (500 MHz, CDCl₃): δ = 7.46 (m, 10H, Ph-*H*), 1.29 (s, 8H, CH₂) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 135.0 (*o*-*C*), 132.9 (i-*C*), 130.3 (*p*-*C*), 128.5 (*m*-*C*), 17.6 (CH₂SiCl₃), 3.8 (Ph₂SiCH₂) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 12.9 (*Si*Cl₃), -3.4 (Ph₂Si) ppm. EI-MS (70 eV): *m*/*z* [assignments] = 505.9, 345.0 [M - (CH₂CH₂SiCl₃)]⁺, 266.9, 217.0, 181.0, 165.0, 134.9, 105.0.

General procedure for fluorination

In a glove box chlorosilanes **3–8** were dissolved in *n*-hexane (2–5 mL) in a glove box. Antimony trifluoride (1.2–1.5 eq.) was added and the suspension was stirred for 20 h at ambient temperature. The solid residue was filtered off, and the product was isolated by removing the solvent. Fluorosilanes **11** and **14** were purified by sublimation (10^{-2} mbar, 80 °C) and isolated as colorless crystalline solids.

Bis(fluorodimethylsilylvinyl)diphenylsilane (9). Yield: 987 mg (94%). ¹H NMR (500 MHz, CDCl₃): δ = 7.43 (m, 10H, Ph-*H*), 7.12 (d, ³*J*_{H,H} = 22.8 Hz, 2H, Ph₂SiC*H*), 6.71 (dd, ³*J*_{H,H} = 22.8 Hz, ³*J*_{F,H} = 2.8 Hz, 2H, CHSiFMe₂), 0.33 (d, ³*J*_{F,H} = 7.3 Hz, 12H, CH₃) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 152.1 (d, ²*J*_{F,C} = 16.4 Hz, CHSiFMe₂), 147.7 (d, ³*J*_{F,C} = 2.6 Hz, Ph₂SiC*H*), 135.8 (*o*-*C*), 133.4 (i-*C*), 130.0 (*p*-*C*), 128.2 (*m*-*C*), -1.3 (d, ²*J*_{F,C} = 15.6 Hz, CH₃) ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ = -162.1 (dsept, ³*J*_{F,H} = 7.3 Hz, ³*J*_{F,H} = 2.8 Hz, CHSiFMe₂) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 17.7 (d, ¹*J*_{Si,F} = 277.6 Hz, *Si*FMe₂), -21.8 (Ph₂Si) ppm. EI-MS (70 eV): *m*/*z* [assignments] = 388.1, 285.1, 234.1, 183.1, 135.1, 105.0, 77.0. HRMS (EI, 70 eV): calculated for C₂₀H₂₆F₂Si₃⁺: 388.13049; measured: 388.13005; dev. [ppm]: 1.13, dev. [mmu]: 0.44.

Bis(difluoromethylsilylvinyl)diphenylsilane (10). Yield: 1.21 g (93%). ¹H NMR (500 MHz, CDCl₃): δ = 7.44 (m, 10H, Ph-*H*), 7.36 (d, ³*J*_{H,H} = 23.0 Hz, 2H, Ph₂SiC*H*), 6.54 (dt, ³*J*_{H,H} = 23.0 Hz, ³*J*_{F,H} = 2.4 Hz, 2H, CHSiF₂Me), 0.47 (t, ³*J*_{F,H} = 6.1 Hz, 6H, CH₃) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 152.7 (t, ³*J*_{F,C} = 2.7 Hz, Ph₂SiCH), 144.9 (t, ²*J*_{F,C} = 19.5 Hz, CHSiF₂Me), 135.8 (*o*-C), 131.7 (*p*-C), 130.4 (i-C), 128.4 (*m*-C), -4.8 (t, ²*J*_{F,C} = 17.0 Hz, CH₃) ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ = -137.1 (dq, ³*J*_{F,H} = 6.1 Hz, ³*J*_{F,H} = 2.4 Hz, CHSiF₂Me) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -16.1 (t, ¹*J*_{Si,F} = 291.6 Hz, *Si*F₂Me), -20.9 (Ph₂Si) ppm. EI-MS (70 eV): *m*/z [assignments] = 396.1, 381.1, 318.0, 289.1, 238.1, 201.1, 183.1, 145.1, 105.0, 81.0. HRMS (EI, 70 eV): calculated for $C_{18}H_{20}F_4Si_3^+$: 396.08035; measured: 396.08064; dev. [ppm]: 0.73, dev. [mmu]: 0.29.

Bis(trifluorosilylvinyl)diphenylsilane (11). Yield: 970 mg (86%). ¹H NMR (500 MHz, CDCl₃): δ = 7.67 (d, ³J_{H,H} = 23.1 Hz, 2H, Ph₂SiCH), 7.47 (m, 10H, Ph-*H*), 6.39 (dq, ³J_{H,H} = 23.1 Hz, ³J_{F,H} = 3.4 Hz, 2H, CHSiF₃) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 158.8 (Ph₂SiCH), 135.7 (*o*-*C*), 134.4 (q, ²J_{F,C} = 25.3 Hz, CHSiF₃), 131.0 (*p*-*C*), 129.9 (i-*C*), 128.7 (*m*-*C*) ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ = -141.5 (d, ³J_{F,H} = 3.4 Hz CHSiF₃) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -20.2 (Ph₂Si), -78.1 (q, ¹J_{Si,F} = 269.3 Hz, SiF₃) ppm. EI-MS (70 eV): *m*/z [assignments] = 404.1, 326.0, 293.1, 242.0, 216.0, 183.1, 150.0, 105.0. HRMS (EI, 70 eV): calculated for C₁₆H₁₄F₆Si₃⁺: 404.03020; measured: 404.02995; dev. [ppm]: 0.62, dev. [mmu]: 0.25.

Bis(fluorodimethylsilylethyl)diphenylsilane (12). Yield: 624 mg (97%). ¹H NMR (500 MHz, CDCl₃): δ = 7.54 (m, 4H, Ph-*H*), 7.41 (m, 6H, Ph-*H*), 1.13 (m, 4H, Ph₂SiC*H*₂), 0.65 (m, 4H, C*H*₂SiFMe₂), 0.25 (d, ³*J*_{F,H} = 7.5 Hz, 12H, C*H*₃) ppm. ¹³C {¹H} NMR (125 MHz, CDCl₃): δ = 135.6 (i-*C*), 135.2 (*o*-*C*), 129.6 (*p*-*C*), 128.2 (*m*-*C*), 8.7 (d, ²*J*_{F,C} = 14.2 Hz, C*H*₂SiFMe₂), 2.8 (Ph₂SiCH₂), -1.9 (d, ²*J*_{F,C} = 15.0 Hz, CH₃) ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ = -163.0 (m, CHSiFMe₂) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 33.1 (d, ¹*J*_{Si,F} = 280.1 Hz, *Si*FMe₂), -3.4 (Ph₂S*i*) ppm. EI-MS (70 eV): *m*/*z* [assignments] = 377.1, 287.1 [M - (CH₂CH₂SiFMe₂)]⁺, 209.1, 197.1, 183.1, 147.1, 121.1, 105.0.

Bis(difluoromethylsilylethyl)diphenylsilane (13). Yield: 862 mg (quant). ¹H NMR (500 MHz, CDCl₃): δ = 7.48 (m, 4H, Ph-*H*), 7.41 (m, 6H, Ph-*H*), 1.14 (m, 4H, Ph₂SiCH₂), 0.69 (m, 4H, CH₂SiF₂Me), 0.32 (t, ³J_{F,H} = 6.3 Hz, 6H, CH₃) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 135.1 (o-C), 134.2 (i-C), 129.9 (p-C), 128.3 (m-C), 5.8 (t, ²J_{F,C} = 15.6 Hz, CH₂SiF₂Me), 1.9 (Ph₂SiCH₂), -4.8 (t, ²J_{F,C} = 16.3 Hz, CH₃) ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ = -137.5 (dq, ³J_{F,H} = 11.3 Hz, ³J_{F,H} = 5.8 Hz, CH₂SiF₂Me) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 2.4 (t, ¹J_{Si,F} = 299.0 Hz, *Si*F₂Me), -3.0 (Ph₂Si) ppm. EI-MS (70 eV): *m/z* [assignments] = 385.1, 291.1 [M - (CH₂CH₂SiF₂Me)]⁺, 233.0, 201.1, 183.1, 121.1, 105.0, 81.0.

Bis(trifluorosilylethyl)diphenylsilane (14). Yield: 1.42 g (89%). ¹H NMR (500 MHz, CDCl₃): δ = 7.45 (m, 10H, Ph*H*), 1.23 (m, 4H, Ph₂SiCH₂), 0.88 (m, 4H, CH₂SiF3) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 135.0 (*o*-*C*), 132.6 (i-*C*), 130.4 (*p*-*C*), 128.5 (*m*-*C*), 2.0 (Ph₂SiCH₂), -0.3 (q, ²J_{F,C} = 19.7 Hz, CH₂SiF₃) ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ = -139.6 (t, ³J_{F,H} = 2.8 Hz CH₂SiF₃) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -2.9 (Ph₂Si), -59.8 (q, ¹J_{Si,F} = 286.0 Hz, SiF₃) ppm. EI-MS (70 eV): *m*/*z* [assignments] = 389.1, 295.1 [M - (CH₂CH₂SiF₃)]⁺, 217.0, 183.1, 150.0, 105.0.

General procedure for the conversion of fluorosilanes 11, 14 and potassium fluoride 18-crown-6 complexes

Spray-dried potassium fluoride (225 mg, 3.87 mmol) and 18-crown-6 (1.00 g, 3.78 mmol) were dissolved in dichloromethane and stirred overnight at ambient temperature. The suspension was filtered, and the solvent was removed from the filtrate under reduced pressure. In a glove box fluorosilane and a potassium fluoride 18-crown-6 mixture (1 or 2 eq.) were dissolved in dichloromethane. The silicate complex was isolated by removing the solvent after stirring for several hours.

[K-18-crown-6]⁺**[Ph₂Si(CHCHSiF₃)(CHCHSiF₄)]**⁻ (15). ¹H NMR (500 MHz, CDCl₃): δ = 7.57 (d, ³*J*_{H,H} = 22.7 Hz, 2H, Ph₂SiC*H*), 7.44 (m, 10H, Ph-*H*), 6.48 (d, ³*J*_{H,H} = 22.7 Hz, 2H, CHSiF_x), 3.58 (s, OCH₂) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 163.2 (Ph₂SiCH), 135.8 (*o*-*C*), 132.2 (i-*C*), 130.4 (br, CHSiF_x), 130.2 (*p*-*C*), 128.2 (*m*-*C*), 70.2 (OCH₂) ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ = -137.6 (s(br), SiF_x) ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -21.4 (Ph₂Si), (SiF_x not observable) ppm. Elemental analysis calcd (%) for C₂₈H₃₈F₇KO₆Si₃ (*M*_r = 726.94): C 46.26, H 5.27; found: C 46.27, H 5.30.

2[K-18-crown-6]⁺[**Ph₂Si(CHCHSiF₄)₂]**²⁻ (**16**). ¹H NMR (500 MHz, CDCl₃): δ = 7.56 (m, 4H, *o*-Ph-*H*), 7.40 (d, ³*J*_{H,H} = 22.0 Hz, 2H, Ph₂SiC*H*), 7.24 (m, 6H, *m*-Ph-*H*, *p*-Ph-*H*), 6.62 (d(br), ³*J*_{H,H} = 21.9 Hz, 2H, CHSiF₄), 3.58 (s, OCH₂) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 167.9 (Ph₂SiCH₂), 148.4 (br, CHSiF₄), 136.5 (i-*C*), 135.9 (*o*-*C*), 128.7 (*p*-*C*), 127.4 (*m*-*C*), 70.3 (OCH₂) ppm. ¹⁹F NMR (470 MHz, CDCl₃): -121.5 [s(br), SiF₄] ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -24.2 (Ph₂Si), -129.6 (SiF₄) ppm. Elemental analysis calcd (%) for C₄₀H₆₂F₈K₂O₁₂Si₃ (*M*_r = 1049.35): C 45.78, H 5.96; found: C 44.289, H 5.98.

[K-18-crown-6]⁺[Ph₂Si(CH₂CH₂SiF₃)(CH₂CH₂SiF₄)][−] (17). ¹H NMR (500 MHz, CDCl₃): \delta = 7.41 (m, 10H, Ph-*H***), 3.57 (s, OCH₂), 1.27 (m, 4H, Ph₂SiCH₂), 0.83 (m, 4H, CH₂SiF_x) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): \delta = 135.2 (***o***-***C***), 129.4 (***p***-***C***), 128.0 (***m***-***C***), 70.3 (OCH₂), 3.5 (br, Ph₂SiCH₂) ppm (i-***C* **not observed due to overlap with** *o***-***C***; CH₂SiF_x not observed due to line broadening). ¹⁹F NMR (470 MHz, CDCl₃): -131.4 [s(br), SiF_x] ppm. ²⁹Si{¹H} NMR (99 MHz, CDCl₃): \delta = −3.4 (Ph₂Si), (***SiF_x* **not observed) ppm. Elemental analysis calcd (%) for C₂₈H₄₂F₇KO₆Si₃ (***M***_r = 730.97): C 46.01, H 5.79; found: C 46.02, H 6.01.**

2[K-18-crown-6]⁺[Ph₂Si(CH₂CH₂SiF₄)₂]²⁻ (18). ¹H NMR (500 MHz, CDCl₃): δ = 7.52 (m, 4H, *o*-Ph-*H*), 7.20 (m, 6H, *m*-Ph-*H*, *p*-Ph-*H*), 3.58 (s, OC*H*₂), 1.27 (m, 4H, Ph₂SiC*H*₂), 0.74 [m(br), 4H, C*H*₂SiF₄] ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 138.4 (i-*C*), 135.4 (*o*-*C*), 128.3 (*p*-*C*), 127.3 (*m*-*C*), 70.3 (OCH₂), 8.5 (br, CH₂SiF₄), 6.2 (Ph₂SiCH₂) ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ = -4.3 (Ph₂Si), -112.0 (*Si*F₄) ppm. Elemental analysis calcd (%) for C₄₀H₆₆F₈K₂O₁₂Si₃ (*M*_r = 1053.39): C 45.61, H 6.32; found: C 44.43, H 6.25.

General procedure for the conversion of fluorosilanes 11, 14 and potassium fluoride [2.2.2]cryptand complexes

Spray-dried potassium fluoride (55 mg, 0.95 mmol) and [2.2.2] cryptand (100 mg, 0.27 mmol) were dissolved in acetone and stirred 3 d at ambient temperature. The suspension was filtered, and the solvent was removed from the filtrate under reduced pressure. ¹H NMR (300 MHz, acetone- d_6): $\delta = 3.64$ (s, 12H, CH_2), 3.61 (m, 12H, CH_2), 2.61 (m, 12H, CH_2) ppm. ¹⁹F NMR (282 MHz, acetone- d_6): $\delta = -109.2$ ppm. Fluorosilane and potassium fluoride [2.2.2]cryptand mixture (1 or 2 eq.)

Table 7	Crystallographic	data for 1	5 11 14	4 15	20 and 22
Tuble /	crystattographic	autu ioi 1,	J, 11, 1	T, 1 3,	

	1	3	5	11	14	15	17	20	22
Empirical formula	C ₁₆ H ₁₂ Si	C ₂₀ H ₂₆ Cl ₂ Si ₃	C ₁₆ H ₁₄ Cl ₆ Si ₃	$C_{16}H_{14}F_6Si_3$	C16H18F6Si3	C ₂₈ H ₃₈ F ₇ KO ₆ Si ₃	C ₂₈ H ₄₂ F ₇ KO ₆ Si ₃	C ₅₂ H ₈₆ F ₈ K ₂ N ₄ O ₁₂ Si ₃	C ₅₂ H ₉₀ F ₈ K ₂ N ₄ O ₁₂ Si ₃
M _r	232.35	421.58	503.26	404.54	408.57	726.95	730.98	1273.71	1277.74
F(000)	488	888	1016	824	840	756	764	1348	1356.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	C2/c	C2/c	$P2_1/c$	$P2_1/n$	P2 ₁	$P2_1$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.06686(12)	17.3643(4)	17.2081(9)	6.69282(16)	9.58517(10)	9.6707(3)	9.62226(18)	11.25235(13)	11.42848(16)
b Å	7.54672(9)	11.5112(3)	11.5831(8)	12.4642(2)	15.67457(13)	14.7072(3)	14.66422(19)	14.6618(2)	14.5458(2)
c [Å]	19.5187(2)	11.4420(3)	11.3044(7)	22.3387(4)	13.23279(17)	12.2271(3)	12.5895(2)	20.6823(2)	20.6353(3)
α [[] °]	90	90	90	90	90	90	90	102.4812(10)	101.0019(12)
βΰĪ	101.1855(13)	90.416(3)	90.810(5)	98.414(2)	109.1776(12)	100.137(3)	99.8129(18)	98.9460(9)	99.0164(12)
γ [°]	90	90	90	90	90	90	90	105.1347(11)	106.2033(12)
V[Å ³]	1310.19(3)	2287.02(10)	2253.0(2)	1843.44(7)	1877.81(4)	1711.91(8)	1750.43(5)	3133.60(7)	3152.30(8)
Z	4	4	4	4	4	2	2	2	2
$\rho_{\rm calcd.} [\rm g \ \rm cm^{-3}]$	1.178	1.224	1.484	1.458	1.445	1.410	1.387	1.350	1.346
Radiation [Å]	0.71073	0.71073	1.54184	1.54184	1.54184	1.54184	1.54184	0.71073	1.54184
$\mu \left[\text{mm}^{-1} \right]^{-1}$	0.153	0.443	8.486	2.896	2.843	3.056	2.990	0.291	2.587
$2\theta_{\rm max}$ [°]	60.04	52.78	133.94	144.25	143.98	143.98	144.0	60.16	144.7
Index range h	$-12 \le h \le 12$	$-21 \le h \le 21$	$-20 \le h \le 18$	$-8 \le h \le 8$	$-11 \le h \le 11$	$-11 \le h \le 10$	$-11 \le h \le 11$	$-15 \le h \le 15$	$-14 \le h \le 14$
Index range k	$-10 \le k \le 10$	$-14 \le k \le 14$	$-9 \le k \le 13$	$-15 \le k \le 15$	$-19 \le k \le 19$	$-18 \le k \le 18$	$-18 \le k \le 18$	$-20 \le k \le 20$	$-17 \le k \le 17$
Index range <i>l</i>	$-27 \le l \le 27$	$-14 \le l \le 14$	$-13 \le l \le 13$	$-27 \le l \le 27$	$-16 \le l \le 16$	$-15 \le l \le 15$	$-15 \le l \le 15$	$-29 \le l \le 29$	$-25 \le l \le 25$
Refl. collected	73 396	44 651	7654	28 265	53 527	30 331	31 114	183 781	68 977
Indep. refl.	3827	2333	2008	3633	3697	6734	6885	18 403	12 436
R _{int}	0.0315	0.0814	0.0427	0.0471	0.0189	0.0528	0.0369	0.0333	0.0252
Obs. refl., $I > 2\sigma(I)$	3646	2003	1865	3184	3621	6155	6665	16 083	11 890
Parameters	154	116	117	258	226	417	443	1000	959
$R_1, I > 2\sigma(I)$	0.0318	0.0323	0.0595	0.0390	0.0284	0.0425	0.0466	0.0368	0.0308
$wR_2, I \ge 2\sigma(I)$	0.0922	0.0826	0.1419	0.1000	0.0708	0.1072	0.1284	0.0899	0.0802
R_1 (all data)	0.0333	0.0383	0.0630	0.0450	0.0288	0.0478	0.0476	0.0435	0.0321
wR ₂ (all data)	0.0932	0.0848	0.1454	0.1048	0.0711	0.1116	0.1299	0.0935	0.0813
GoF	1.133	1.076	1.079	1.045	1.032	1.038	1.032	1.036	1.048
$ ho_{ m max}/ ho_{ m min} \left[e { m \AA}^{-3} ight]$	0.42 / -0.22	0.40 / -0.28	1.12 / -0.71	0.42 / -0.35	0.68 / -0.45	0.29/-0.72	0.50/-0.29	0.71/-0.78	0.40/-0.41
Remarks	_	_	_	a	_	D	С	a	_
CCDC number	1520262	1520263	1520264	1520265	1520266	1520267	1520268	1520269	1520270

Remarks: ^{*a*} Disorder of F(1), F(2) and F(3) on two positions (58:42); disorder of Si(3), F(4), F(5), F(6) and C(4) on two positions (83:17). ^{*b*} Refined as a two component inversion twin (BASF 0.497); disorder of F(5), F(6) and F(7) on two positions (81:19). ^{*c*} Disorder of the entire silicate anion with ratio 83:17. ^{*d*} Disorder of F(5), F(6), F(7) and F(8) over two sites (54:46); disorder of C(1) to C(6) over two sites (67:37); disorder of the second cation excluding K(2), O(11) and O(12) over two sites (75:25).

were dissolved in acetone- d_6 and sonicated in a Young NMR tube for 30 min.

[K-[2.2.2]cryptand]⁺[Ph₂Si(CHCHSiF₃)(CHCHSiF₄)]⁻ (19). ¹H NMR (500 MHz, acetone-*d*₆): δ = 7.54 (m, 4H, *o*-Ph-*H*), 7.36 (d, ³*J*_{H,H} = 22.0 Hz, 2H, Ph₂SiC*H*), 7.36 (m, 6H, *m*-Ph-*H*, *p*-Ph-*H*), 6.62 (d, ³*J*_{H,H} = 22.0 Hz, 2H, CHSiF_x), 3.63 (s, 12H, CH₂), 3.59 (m, 12H, CH₂), 2.60 (m, 12H, CH₂) ppm. ¹³C{¹H} NMR (125 MHz, acetone-*d*₆): δ = 162.9 (Ph₂SiCH), 137.0 (i-C), 136.4 (*o*-C), 129.8 (*p*-C), 128.5 (*m*-C), 71.2 (CH₂), 68.4 (CH₂), 54.7 (CH₂), (CHSiF_x not observable) ppm. ¹⁹F NMR (470 MHz, acetone-*d*₆): δ = -120.1 [s(br), SiF_x] ppm. ²⁹Si{¹H} NMR (99 MHz, acetone-*d*₆): δ = -23.5 (Ph₂Si), (SiF_x not observable) ppm. Elemental analysis calcd (%) for C₃₄H₅₀F₇KN₂O₆Si₃ (*M*_r = 839.11): C 48.67, H 6.01, N 3.34; found: C 49.05, H 6.39, N 3.22.

 $\begin{aligned} & \{ \text{K-}[2.2.2] \text{cryptand} \}^{+} [\text{Ph}_2 \text{Si}(\text{CHCHSiF}_4)]^{2-} \quad (20). \quad ^{1}\text{H} \quad \text{NMR} \\ & (500 \text{ MHz, acctone-} d_6): \delta = 7.56 \ (\text{m}, 4\text{H}, o\text{-Ph-}H), 7.32 \ (\text{d}, \, ^3J_{\text{H},\text{H}} = 21.9 \ \text{Hz}, 2\text{H}, \text{Ph}_2 \text{Si}(\text{CH}), 7.32 \ (\text{m}, 6\text{H}, m\text{-Ph-}H, p\text{-Ph-}H), 6.68 \ (\text{d}, \, ^3J_{\text{H},\text{H}} = 21.9 \ \text{Hz}, 2\text{H}, \text{CH}_2 \text{Si}(\text{CH}), 3.62 \ (\text{s}, 12\text{H}, \text{CH}_2), 3.58 \ (\text{m}, 12\text{H}, \text{CH}_2), 2.58 \ (\text{m}, 12\text{H}, \text{CH}_2) \ \text{ppm.} \quad ^{13}\text{C}\{^{1}\text{H}\} \ \text{NMR} \ (125 \ \text{MHz}, acctone-d_6): \delta = 160.9 \ (\text{Ph}_2 \text{Si}(\text{CH}), 146.4 \ (\text{br}, \text{CHSiF}_4), 138.2 \ (\text{i-}C), 136.5 \ (o-C), 129.4 \ (p-C), 128.2 \ (m-C), 71.2 \ (CH_2), 68.4 \ (CH_2), 54.6 \ (CH_2) \ \text{ppm.} \quad ^{19}\text{F} \ \text{NMR} \ (470 \ \text{MHz}, acctone-d_6): \delta = -119.8 \ (\text{s}, \text{SiF}_4) \ \text{ppm.} \quad ^{29}\text{Si}\{^{1}\text{H}\} \ \text{NMR} \ (99 \ \text{MHz}, acctone-d_6): \delta = -23.5 \ (\text{Ph}_2 Si), -130.2 \ (SiF_4) \ \text{ppm.} \ \text{Elemental analysis calcd} \ (\%) \ \text{for} C_{52}\text{H}_{86}\text{F}_8\text{K}_2\text{N}_4\text{O}_{12}\text{Si} \ (M_r = 1273.70): C \ 49.03, \ \text{H} \ 6.81, \ \text{N} \ 4.40; \ \text{found: C} \ 49.34, \ \text{H} \ 6.98, \ \text{N} \ 4.40. \end{aligned}$

[K-[2.2.2]cryptand]⁺[Ph₂Si(CH₂CH₂SiF₃)(CH₂CH₂SiF₄)]⁻ (21). ¹H NMR (500 MHz, acetone-*d*₆): δ = 7.56 (m, 4H, *o*-Ph-*H*), 7.34 (m, 6H, *m*-Ph-*H*, *p*-Ph-*H*), 3.62 (s, 12H, CH₂), 3.58 (m, 12H, CH₂), 2.59 (m, 12H, CH₂), 1.29 (m, 4H, Ph₂SiCH₂), 0.75 (m, 4H, CH₂SiF_x) ppm. ¹³C{¹H} NMR (125 MHz, acetone-*d*₆): δ = 139.4 (i-*C*), 136.0 (*o*-*C*), 129.1 (*p*-*C*), 128.2 (*m*-*C*), 71.2 (CH₂), 68.3 (CH₂), 54.6 (CH₂), 9.4 (CHSiF_x), 6.7 (Ph₂SiCH₂) ppm. ¹⁹F NMR (470 MHz, acetone-*d*₆): δ = -123.7 [s(br), SiF_x] ppm. ²⁹Si{¹H} NMR (99 MHz, acetone-*d*₆): δ = -3.9 (Ph₂Si), (SiF_x not observed) ppm. Elemental analysis calcd (%) for C₃₄H₅₄F₇KN₂O₆Si₃ (*M*_r = 843.15): C 48.43, H 6.46, N 3.32; found: C 48.48, H 6.87, N 3.80.

2{K-[2.2.2]cryptand}⁺[Ph₂Si(CH₂CH₂SiF₄)]²⁻ (22). ¹H NMR (500 MHz, acetone- d_6): δ = 7.57 (m, 4H, *o*-Ph-*H*), 7.29 (m, 6H, *m*-Ph-*H*, *p*-Ph-*H*), 3.62 (s, 12H, CH₂), 3.58 (m, 12H, CH₂), 2.58 (m, 12H, CH₂), 1.28 (m, 4H, Ph₂SiCH₂), 0.65 (m, 4H, CH₂SiF₄) ppm. ¹³C{¹H} NMR (125 MHz, acetone- d_6): δ = 140.0 (i-*C*), 136.0 (*o*-*C*), 128.9 (*p*-*C*), 128.1 (*m*-*C*), 71.2 (*C*H₂), 68.3 (*C*H₂), 54.6 (*C*H₂), 10.4 (*C*HSiF₄), 7.4 (Ph₂SiCH₂) ppm. ¹⁹F NMR (470 MHz, acetone- d_6): δ = -117.3 (s, SiF₄) ppm. ²⁹Si{¹H} NMR (99 MHz, acetone- d_6): δ = -4.1 (Ph₂Si), -113.6 (*S*iF₄) ppm. Elemental analysis calcd (%) for C₅₂H₉₀F₈K₂N₄O₁₂Si₃ (M = 1277.73): C 48.88, H 7.10, N 4.38; found: C 48.65, H 7.16, N 4.31.

Crystallography

Suitable crystals of compounds 1, 3, 5, 11, 14, 15, 17, 20 and 22 were obtained by slow evaporation of saturated solutions of THF (1), *n*-hexane (3, 5), Et_2O (11, 14), dichloromethane (15,

17) and acetone (20, 22). They were coated with paratone-N oil, selected, mounted on a glass fiber and transferred onto the goniometer and into the cryostream of the diffractometer. Data collections were performed at 100.0(2) K on a SuperNova diffractometer, using monochromated Cu-K α radiation for compounds 5, 11, 14, 15, 17 and 22 and Mo-K α radiation for compounds 1, 3 and 20.

Using Olex2 the structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97).³⁹ Crystal and refinement details, as well as CCDC numbers are provided in Table 7. CCDC 1520262–1520270 contain the supplementary crystallographic data for this paper.

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Notes and references

- 1 C. J. Pedersen, J. Am. Chem. Soc., 1967, 89, 7017-7036.
- 2 (a) J.-H. Lamm, J. Horstmann, J. H. Nissen, J.-H. Weddeling, B. Neumann, H.-G. Stammler and N. W. Mitzel, *Eur. J. Inorg. Chem.*, 2014, 4294–4301;
 (b) J. Chmiel, B. Neumann, H.-G. Stammler and N. W. Mitzel, *Chem. Eur. J.*, 2010, 16, 11906–11914.
- 3 (a) M. M. G. Antonisse and D. N. Reinhoudt, *Chem. Commun.*, 1998, 443–447; (b) J. W. Steed, *Chem. Soc. Rev.*, 2009, 38, 506–519; (c) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, 40, 486–516.
- 4 (a) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge and F. P. Gabbaï, Chem. Rev., 2010, 110, 3958-3984; (b) T. W. Hudnall, C.-W. Chiu and F. P. Gabbaï, Acc. Chem. Res., 2009, 42, 388-397; (c) H. Zhao and F. P. Gabbaï, Organometallics, 2012, 31, 2327-2335; (d) Z. Li, K. Chansaenpak, S. Liu, C. R. Wade, P. S. Conti and F. P. Gabbaï, MedChemComm, 2012, 3, 1305-1308; (e) J. M. Koomen, J. E. Lucas, M. R. Haneline, J. D. Beckwith King, F. P. Gabbaï and D. H. Russell, Int. J. Mass Spectrom., 2003, 225, 225-231; (f) H. Zhao and F. P. Gabbaï, Nat. Chem., 2010, 2, 984-990; (g) M. Hirai and F. P. Gabbaï, Angew. Chem., Int. Ed., 2015, 54, 1205-1209; (h) J. S. Jones, C. R. Wade and F. P. Gabbaï, Organometallics, 2015, 34, 2647-2654; (i) M. Hirai, M. Myahkostupov, F. N. Castellano and F. P. Gabbaï, Organometallics, 2016, 35, 1854-1860.
- 5 D. Brondani, F. H. Carré, R. J. P. Corriu, J. J. E. Moreau and M. Wong Chi Man, Angew. Chem., Int. Ed. Engl., 1996, 35, 324.
- 6 M. E. Jung and H. Xia, Tetrahedron Lett., 1988, 29, 297–300.

- 7 K. Tamao, T. Hayashi and Y. Ito, *Organometallics*, 1992, **11**, 2099–2114.
- 8 S. Aoyagi, K. Tanaka and Y. Takeuchi, *J. Chem. Soc., Perkin. Trans.* 2, 1994, 1549–1553.
- 9 R. Altmann, O. Gausset, D. Horn, K. Jurkschat and M. Schürmann, Organometallics, 2000, 19, 430–443.
- 10 (a) K. Tamao, T. Hayashi and Y. Ito, J. Organomet. Chem., 1996, 506, 85–91; (b) Y. Kim, M. Kim and F. P. Gabbaï, Org. Lett., 2010, 12, 600–602; (c) A. Kawachi, A. Tani, J. Shimada and Y. Yamamoto, J. Am. Chem. Soc., 2008, 130, 4222–4223.
- 11 D. Dakternieks, A. Duthie, R. Altmann, K. Jurkschat and M. Schürmann, *Organometallics*, 1998, **17**, 5858–5866.
- 12 (a) R. Panisch, M. Bolte and T. Müller, J. Am. Chem. Soc.,
 2006, 128, 9676–9682; (b) C. L. Dorsey and F. P. Gabbaï,
 Organometallics, 2008, 27, 3065–3069.
- D. Dakternieks, A. Duthie, R. Altmann, K. Jurkschat and M. Schürmann, Organometallics, 1997, 16, 5716–5723.
- 14 A. S. Wendji, C. Dietz, S. Kühn, M. Lutter, D. Schollmeyer, W. Hiller and K. Jurkschat, *Chem. – Eur. J.*, 2016, 22, 404–416.
- 15 (a) E. Weisheim, B. Neumann, H.-G. Stammler and N. W. Mitzel, Z. Anorg. Allg. Chem., 2016, 642, 329–334;
 (b) E. Weisheim, L. Büker, B. Neumann, H.-G. Stammler and N. W. Mitzel, Dalton Trans., 2016, 45, 198–207;
 (c) E. Weisheim, C. G. Reuter, P. Heinrichs, Y. V. Vishnevskiy, A. Mix, B. Neumann, H.-G. Stammler and N. W. Mitzel, Chem. – Eur. J., 2015, 21, 12436–12448;
 (d) E. Weisheim, H.-G. Stammler and N. W. Mitzel, Z. Naturforsch., B: Chem. Sci., 2016, 71, 77–79.
- 16 (a) J.-H. Lamm, J. Horstmann, H.-G. Stammler, N. W. Mitzel, Y. A. Zhabanov, N. V. Tverdova, A. A. Otlyotov, N. I. Giricheva and G. V. Girichev, *Org. Biomol. Chem.*, 2015, 13, 8893–8905; (b) A. Nieland, J.-H. Lamm, A. Mix, B. Neumann, H.-G. Stammler and N. W. Mitzel, *Z. Anorg. Allg. Chem.*, 2014, 640, 2484–2491; (c) J.-H. Lamm, J. Glatthor, J.-H. Weddeling, A. Mix, J. Chmiel, B. Neumann, H.-G. Stammler and N. W. Mitzel, *Org. Biomol. Chem.*, 2014, 12, 7355–7365.
- 17 E. Weisheim, A. Schwartzen, L. Kuhlmann, B. Neumann, H.-G. Stammler and N. W. Mitzel, *Eur. J. Inorg. Chem.*, 2016, 16, 1257–1266.
- 18 (a) U. Krüerke, J. Organomet. Chem., 1970, 21, 83–90;
 (b) S. D. Rosenberg, J. J. Walburn, T. D. Stankovich,
 A. E. Balint and H. E. Ramsden, J. Org. Chem., 1957, 22, 1200–1202; (c) M. Fischer and R. Tacke, Organometallics, 2013, 32, 7181–7185.
- 19 Dichlorodiphenylsilane (97%) must be distilled freshly to inhibit the formation of any volatile byproducts. The cheaper reaction route is a single deprotonation of acetylene gas with *n*-BuLi at -30 °C followed by the addition of dichlorodiphenylsilane in THF. To separate the acetylene from the acetone contained the gas cylinder, we used two -78 °C cooling traps (CAUTION: the traps must not be in order to prohibit the condensation of acetylene and avoid the resulting explosion hazard). However, the use of the Grignard species enhanced the yield from 70 to 91%.

- 20 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 21, 2832–2838.
- 21 (a) A. F. Holleman, E. Wiberg and N. Wiberg, *Lehrbuch der Anorganischen Chemie*, de Gruyter, Berlin, 1985, pp. 91–100;
 (b) G. Dierker, J. Ugolotti, G. Kehr, R. Fröhlich and G. Erker, *Adv. Synth. Catal.*, 2009, 351, 1080–1088.
- A. A. Anisimov, Y. N. Kononevich, A. A. Korlyukov,
 D. E. Arkhipov, E. G. Kononova, A. S. Peregudov,
 O. I. Shchegolikhina and A. M. Muzafarov, *J. Organomet. Chem.*, 2014, 772, 79–83.
- 23 S. W. Carr, M. Motevalli, D. L. Ou and A. C. Sullivan, *J. Mater. Chem.*, 1997, 7, 865–872.
- 24 (a) N. W. Mitzel, P. T. Brain, M. Hofmann, D. W. H. Rankin, R. Schröck and H. Schmidbaur, Z. Naturforsch., 2002, 57B, 202–214; (b) B. F. Johnston, N. W. Mitzel, D. W. H. Rankin, H. E. Robertson, C. Rüdinger and H. Schmidbaur, Dalton Trans., 2005, 2292–2299; (c) J. E. Laska, P. Kaszynski and S. J. Jacobs, Organometallics, 1998, 17, 2018– 2026.
- 25 N. W. Mitzel, K. Vojinovic, T. Foerster, H. E. Robertson,
 K. B. Borisenko and D. W. H. Rankin, *Chem. Eur. J.*, 2005,
 11, 5114–5125.
- 26 (a) B. N. Menshutkin, Zh. Russ. Fiz. Khim. Ova. Chast. Khim., 1911, 43, 1298; (b) W. Smith and G. W. Davis, J. Chem. Soc. Trans., 1882, 41, 411; (c) G. Peyronel, S. Buggani and I. M. Vezzosi, Gazz. Chim. Ital., 1968, 98, 147; (d) G. Bombieri, G. Peyronel and I. M. Vezzosi, Inorg. Chim. Acta, 1972, 6, 349; (e) A. Demalde, A. Mangia, M. Nardelli, G. Pelizzi and M. E. Vidoni Tani, Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem., 1972, 28, 147; (f) J. T. Szyamnski and R. Hulme, Acta. Crystallogr., Sect. B: Struct. Crystallogr. Chem., 1969, 28, 753; (g) S. Pohl, W. Saak and D. Haase, Angew. Chem., 1987, 99, 462, (Angew. Chem., Int. Ed. Engl., 1987, 26, 467); (h) H. Schmidbaur, R. Nowak, B. Huber and G. Müller, Organometallics, 1987, 6, 2266.
- 27 F. H. Carr and E. A. Price, *Biochem. J.*, 1926, 20, 497–501.
- 28 (a) V. Plack, P. Sakhaii, A. Fischer, P. G. Jones, R. Schmutzler, K. Tamao and G.-R. Sun, *J. Organomet. Chem.*, 1998, 553, 111–114; (b) H. Sakurai, Y. Nakadaira, H. Tobita, T. Ito, K. Toriumi and H. Ito, *J. Am. Chem. Soc.*, 1982, 104, 300–302.
- 29 N. Rani, P. Sengupta, A. K. Singh and R. J. Butcher, *Polyhedron*, 2007, **26**, 5477–5483.
- 30 R. Pietschnig and K. Merz, *Chem. Commun.*, 2001, 1210–1211.
- 31 (a) C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, *Chem. Rev.*, 1993, 93, 1371–1448; (b) R. Damrauer, B. O'Connell, S. E. Danahey and R. Simon, *Organometallics*, 1989, 5, 1167–1171; (c) S. Spirk, F. Belaj, M. Nieger, H. Köfeler, G. N. Rechberger and R. Pietschnig, *Chem. Eur. J.*, 2009, 15, 9521–9529.
- 32 Albeit THF was reported to be used, the crystal structure of heptafluorotrisilacyclohexane anion displays a dichloromethane molecule.⁵.

- 33 S. E. Johnson, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1989, **28**, 3182–3189.
- 34 (a) R. Damrauer and S. E. Danahey, *Organometallics*, 1986,
 5, 1490–1494; (b) S. Yamaguchi, S. Akiyama and K. Tamao, *Organometallics*, 1999, 18, 2851–2854; (c) P. D. Price,
 M. J. Bearpark, G. S. McGrady and J. W. Steed, *Dalton Trans.*, 2008, 271–282.
- 35 (a) D. Schomburg, J. Organomet. Chem., 1981, 221, 137–141;
 (b) X. Ou and A. F. Janzen, *Inorg. Chem.*, 1997, 36, 392–395;
 (c) K. Ebata, T. Inada, C. Kabuto and H. Sakurai, J. Am. Chem. Soc., 1994, 116, 3595–3596.
- 36 R. R. Holmes, Chem. Rev., 1996, 96, 927-950.
- 37 (a) B. Dietrich and J. M. Lehn, *Tetrahedron Lett.*, 1973, 15, 1225–1228; (b) S. Yamaguchi, S. Akiyama and K. Tamao, J. Am. Chem. Soc., 2000, 122, 6793–6794.
- 38 We generated {K·[2.2.2]cryptand}⁺F⁻ by using spray dried potassium fluoride and [2.2.2]cryptand in dichloromethane. Albeit the complexation of K⁺ could easily be monitored *via* ¹H NMR spectroscopy, a ¹⁹F NMR resonance could not be detected. The X-ray structure analysis of this compound displays its chloride salt {K·[2.2.2]cryptand}⁺Cl⁻ indicating that an anion exchange took place during the reaction. After preparing the {K·[2.2.2]cryptand}⁺F⁻ salt in acetone we were able to detect a ¹⁹F NMR signal at δ = -109.2 ppm.
- 39 (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339–341; (b) G. N. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 2008, 64, 112–122.