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Structural characterization of hydro-, chloro- and fluoroorganylsilanes with substituents of varying electron withdrawing character

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Abstract: We report on the molecular structure of trimethylsilanes $Si(CH_3)_3X$ in which the substituents X, namely (*Z*)-pentafluoropropen-1-yl, trifluoropropyn-1-yl, pentafluoroethyl, trifluorovinyl, vinyl, propyn-1-yl, di- and trichloromethyl, display electron withdrawing effects of varying strength. The lengths of the bonds between the silicon and the carbon atoms of X correlate with the hybridization of the respective orbitals and the steric demand of X rather than with the electron withdrawing capability. In case of chlorinated substituents dispersion effects seem to shorten the Si-C bond. Furthermore, a route for generating trifluoropropyn-1-yllithium from the cryogen 2,3,3,3-tetrafluoropropene (HFO-1234yf) and *n*-butyllithium is described. Tetrafluoropropen-1-yllithium is slowly formed at −80 °C but even at this temperature spontaneous elimination of LiF occurs. Deprotonation of the formed 3,3,3-trifluoropropyne requires temperatures of above −60 °C leading to trifluoropropyn-1-yllithium which appears as relatively stable at room temperature.

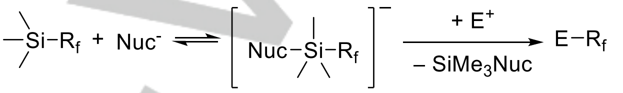
Introduction

Electron withdrawing substituents are imperative in all fields of chemistry. The strength of electron withdrawing effects of the substituents significantly influences the Lewis acidity of molecules. Such substituents are of interest to finetune the Lewis acidic character of catalysts employed in organic[1] and polymer chemistry[2] as well as for the design of frustrated Lewis pairs[3].

The calculation of the C-O bond length of a *para* or *meta* substituted phenolate ion provides a convenient way to classify the strength of this effect. A shortened C-O bond corresponds with an increased electron withdrawing activity of a substituent X. The difference $\Delta(O^-)_{m,p}$ between this bond length $d(XC_6H_4\text{-}O^-)$ and the C-O bond length of the non-substituted phenolate $d(C_6H_5\text{-}O^-)$ provides parameters in good agreement with the well-established Hammett constants.[4]

Due to the high electronegativity of fluorine perfluoroorganyl groups are powerful electron withdrawing substituents. Their transfer is not trivial but over the years efficient methods have been established, for example nucleophilic perfluoroalkylation with various types of organometallic reagents, electrophilic perfluoroalkylation with reagents such as iodonium salts, and radical perfluoroalkylation with iodides.[5]

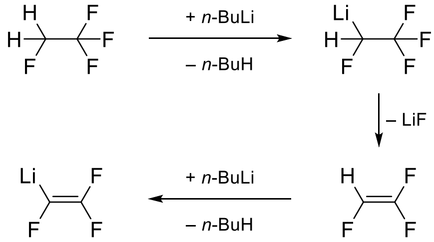
One convenient approach is based upon usage of trimethylperfluoroorganylsilanes, which as mostly stable liquids are easy to handle and often commercially available. They are activated by catalytic amounts of nucleophiles, typically fluoride ions. After activation the perfluoroorganyl groups exhibit nucleophilic character and are smoothly transferred upon electrophilic compounds (Scheme 1).[6]



Scheme 1. Transfer of perfluoroorganyl groups R_f upon electrophilic reagents E^+ using nucleophiles Nuc^- for activation of the respective perfluoroorganylsilane.

One of the preparatively most relevant silanes of this kind is the Ruppert-Prakash reagent, trimethyl(trifluoromethyl)silane. For its preparation tris(diethylamino)phosphane, bromotrifluoromethane and chlorotrimethylsilane are employed. Supposedly the phosphane activates bromotrifluoromethane leading to a trifluoromethanide synthon which reacts with chlorotrimethylsilane under formation of a phosphonium chloride and trimethyl(trifluoromethyl)silane.[7] However, most perfluoroorganylsilanes are nowadays prepared from the respective lithium reagent, provided that it is sufficiently stable, with bromo- or chlorotrimethylsilane under liberation of lithium bromide or chloride as byproduct.

Those lithium reagents have been synthesized by transmetalation and deprotonation processes. Unsatured perfluoroorganyllithium reagents are available either by deprotonation of the corresponding perfluoroalkene or perfluoroalkyne or else by treatment of di- and trihydrofluoroalkanes with appropriate lithium bases. In the latter reactions several deprotonation steps are followed by elimination of lithium fluoride yielding targeted species. The preparation of trifluorovinyllithium via transmetalation from trifluorovinyltin compounds and phenyllithium was first published 1960.[8] However, it is more conveniently accessible by treatment of 1,1,1,2-tetrafluoroethane with two equivalents of *n*-butyllithium.[9] It is conceivable that the initial deprotonation is followed by the elimination of lithium fluoride to yield trifluoroethene which is deprotonated again by *n*-butyllithium affording the final product (Scheme 2).



Scheme 2. Proposed formation of trifluorovinyllithium.

The reaction of trifluorovinyllithium with trimethylbromosilane smoothly affords trimethyl(trifluorovinyl)silane[10] which is utilized for the transfer of the trifluorovinyl group upon electrophilic compounds using catalytic amounts of fluoride[11].

Trifluoropropyn-1-yllithium was generated by deprotonation of 3,3,3-trifluoropropyne with *n*-butyllithium[12] or by treatment of 1,1,1,3,3-pentafluoropropane with three equivalents of *n*-butyllithium[13]. In the latter case three deprotonation steps took place followed by the stepwise elimination of two equivalents of lithium fluoride. Most perfluoroorganyllithium compounds are relatively unstable and require low temperatures to prevent the facile elimination of lithium fluoride. Trifluoropropyn-1-yllithium on the other hand is relatively stable due to the lack of fluorine atoms in *β*-position.[12] As the above-mentioned preparation of trifluorovinyllithium indicates, *β*-fluorine atoms are particularly easy dissociated.

The transfer method via trimethylsilanes is not limited to perfluoroorganyl groups. Trimethyl(trichloromethyl)silane and trimethyl(dichloromethyl)silane serve as a transfer reagents of the trichloromethyl and dichloromethyl groups.[14] Unsatured hydroorganylsilanes such as trimethylvinylsilane are also available for transfer of the respective substituent by electrophilic substitution which might be catalyzed by fluoride ions.[15]

Most of those widely applied trimethylsilanes, however, lack structural characterization. We sought to start filling this gap covering different types of substituents and explore which effects are influencing the structures.

Results and Discussion

We studied easily accessible trimethylsilanes $Si(CH_3)_3X$ with several substituents X. For classification of the strength of the electron withdrawing effect of the substituents X the parameter $\Delta(O^-)_{m,p}$ was used.[4] For that reason the C-O bond lengths of corresponding *para* substituted phenolate ions with those substituents were calculated (Figure 1).

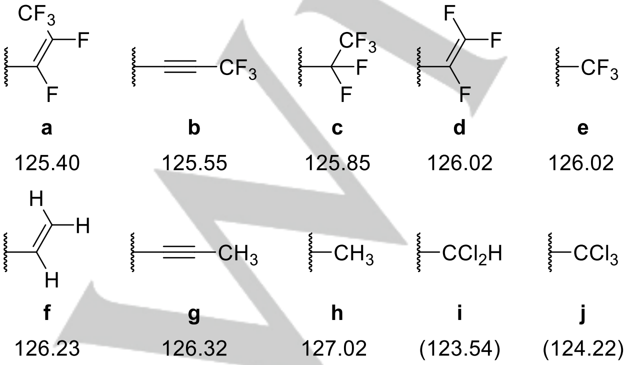
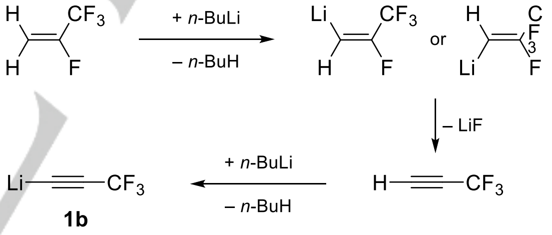


Figure 1. Examined groups **a** to **j** and calculated C-O bond lengths (pm) of the respective *para* substituted phenolate ion $d(XC_6H_4\text{-}O^-)$. Non-substituted phenolate: $d(C_6H_5\text{-}O^-)$=126.91 pm. The calculations were performed on B3LYP/6-311+g(2d,p) level.[16] In case of **i** and **j** the molecule in its optimized structure dissociates into a chloride ion and a corresponding *p*-quinomethane derivative.

Since a shortened C-O bond length correlates with an increased electron withdrawal the (*Z*)-pentafluoropropen-1-yl (**a**) group exerts the strongest electron withdrawing effect of the perfluoroorganyl substituents studied, followed by the trifluoropropyn-1-yl (**b**), pentafluoroethyl (**c**), trifluorovinyl (**d**) and trifluoromethyl (**e**) group. The effect of the last two is virtually identical. Unsurprisingly, the C-O bond lengths of the non-fluorinated analogs are distinctly longer. The unsatured vinyl (**f**) and propyn-1-yl (**g**) groups display electron withdrawing behavior whereas the methyl (**h**) group is electron donating in agreement with common knowledge about inductive effects. In case of the substituents di- and trichloromethyl (**i**, **j**) the molecules in their optimized structure consist of a chloride ion and the corresponding *p*-quinomethane derivative. Therefor the C-O bond lengths are especially short but inadequate to classify the strength of the electron withdrawing effect of substituents **i** and **j**.

The studied silanes were either purchased or prepared from the respective lithium reagents and chlorotrimethylsilane. (*Z*)-pentafluoropropen-1-yllithium[17] (**1a**), pentafluoroethyllithium[18] (**1c**) and trifluorovinyllithium[19] (**1d**) were prepared similar to literature procedures starting from (*Z*)-1,2,3,3,3-pentafluoropropene, pentafluoroethane and 1,1,1,2-tetrafluoroethane. For the generation of trifluoropropyn-1-yllithium (**1b**) the cryogen 2,3,3,3-tetrafluoropropene, also known as HFO-1234yf or R1234yf, was reacted with two equivalents of *n*-butyllithium (Scheme 3).



Scheme 3. Formation of trifluoropropyn-1-yllithium starting from 2,3,3,3-tetrafluoropropene.

NMR spectroscopic monitoring at low temperatures (Figure 2) revealed that trifluoropropyne is slowly formed at −80 °C. Even at this temperature no tetrafluoropropenyllithium was detected. The elimination of lithium fluoride seems to occur nearly instantaneously after the first deprotonation step. Up to −65 °C no trifluoropropyn-1-yllithium (**1b**) was detected. A reaction time of 2 h at −60 °C, however, was sufficient for the completion of both deprotonation steps. Nevertheless, it is unnecessary to maintain that temperature since trifluoropropyn-1-yllithium (**1b**) is relatively stable. Even after one hour at room temperature no apparent decomposition was detected. After two days, however, deterioration of this species was nearly complete. The second deprotonation step seems to happen more readily than the first one since all trifluoropropyne was consumed even though a small amount of tetrafluoropropene was left. For further investigation of the stability of the lithium reagent, **1b** was prepared in diethyl ether, warmed to room temperature and subsequently mixed with chlorotrimethylsilane to afford trimethyl(trifluoropropyn-1-yl)silane (**2b**) (98 % conversion).

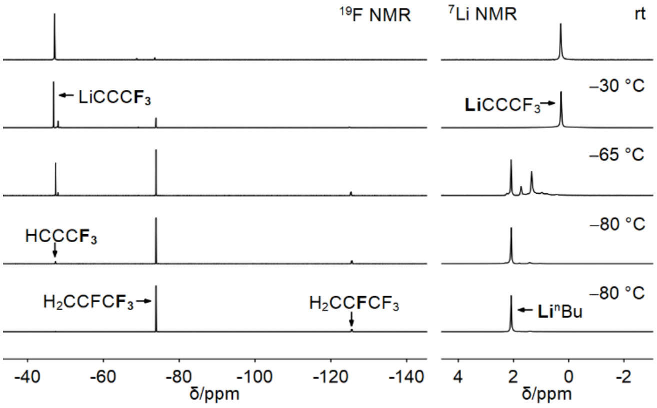


Figure 2. Section of the ^{19}F (left) and ^{7}Li (right) NMR spectra of a reaction mixture of *n*-butyllithium and tetrafluoropropene in diethyl ether at −80 °C (immediately), −80 °C (after 10 min), −65 °C (after 1 h), −30 °C (after 2 h) and room temperature (after 2 ½ h) from bottom to top.

The reaction of lithium reagents **1a-d** with chlorotrimethylsilane in dimethyl ether afforded (*E*)-trimethyl(pentafluoropropen-1-yl)silane (**2a**), trimethyl(trifluoropropyn-1-yl)silane (**2b**), trimethyl(pentafluoroethyl)silane (**2c**) and trimethyl(trifluorovinyl)silane (**2d**). Because of its low boiling point of −24.8 °C[20] dimethyl ether could be easily separated from the silanes (boiling points of **2a**: 94 °C[21], **2b**: 73-74 °C[22], **2c**: 69-71 °C[23], **2d**: 65 °C[10]) whereas the purification of silanes generated in diethyl ether is sometimes effortful.

Suitable crystals for x-ray diffraction studies from fluoroorganylsilanes **2a-d**, trimethylvinylsilane (**2f**), trimethylpropyn-1-ylsilane (**2g**), (dichloromethyl)trimethylsilane (**2i**) and trimethyl(trichloromethyl)silane (**2j**) were obtained by *in situ* crystallization. Their molecular structures and selected bonding parameters are shown in Figure 3 to Figure 10.

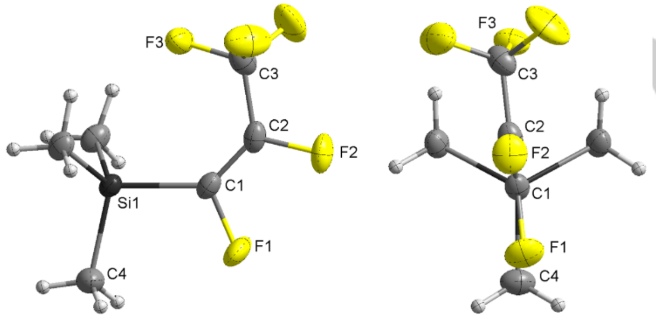


Figure 3. Molecular structure of Si(CH$_3$)$_3$(C$_3$F$_5$) (**2a**) in two different perspectives. Thermal ellipsoids are shown at 50 % probability. The asymmetric unit contains three molecules of which only one is shown for clarity. Selected bond lengths (pm) and angles (°): Si1-C1 192.0(1), Si1-C4 185.7 (1), C1-F1 137.1(1), C2-F2 134.8(1), C3-F3 133.0(1), C1-C2 132.5(2), C2-C3 149.3(2), C1-Si1-C4 102.87(5), Si1-C1-C2 134.92(8), C1-C2-C3 127.82(9), Si1-C1-C2-C3 −2.0(2), C4-Si1-C1-C2 −172.1(1).

Pentafluoropropenylsilane **2a** crystallizes in the triclinic space group *P*-1. F1 and C4 are nearly syn-periplanar.

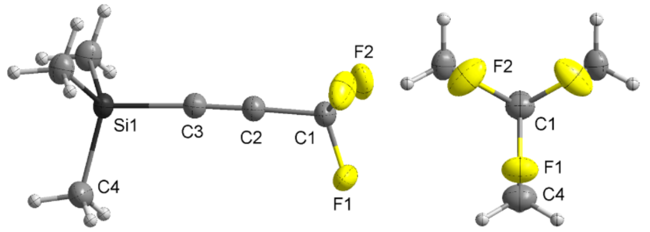


Figure 4. Molecular structure of Si(CH$_3$)$_3$(C$_3$F$_3$) (**2b**) in two different perspectives. Thermal ellipsoids are shown at 50 % probability. Selected bond lengths (pm) and angles (°): Si1-C3 186.5(2), Si1-C4 185.6(3), C1-F1 133.9(3), C1-F2 133.1(2), C1-C2 146.1(3), C2-C3 120.1(3), C3-Si1-C4 105.4(1), C2-C3-Si1 177.2(2), C1-C2-C3 178.3(2).

Trifluoropropynylsilane **2b** crystallizes in the monoclinic space group $P2_1/m$. C4, Si1, C1 and F1 are located on the mirror plane. Contrary to trifluoromethylsilane **2e**, where the fluorine atoms and the methyl groups are in a staggered configuration,[24] in **2b** the eclipsed conformation is favored.

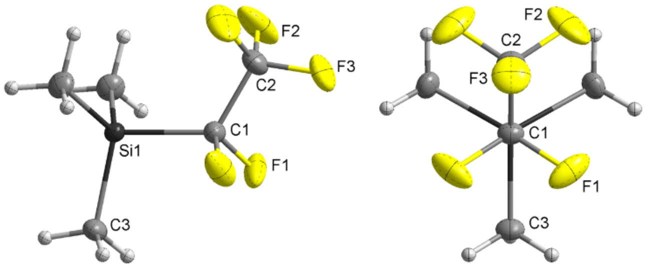


Figure 5. Molecular structure of Si(CH$_3$)$_3$(C$_2$F$_5$) (**2c**) in two different perspectives. Thermal ellipsoids are shown at 50 % probability. Selected bond lengths (pm) and angles (°): Si1-C1 195.1(2), Si1-C3 185.7(1), C1-F1 137.0(1), C2-F2 132.0(2), C2-F3 133.1(2), C1-Si1-C3 101.64(7).

Pentafluoroethylsilane **2c** crystallizes in the orthorhombic space group $Cmc2_1$. C3, Si1, C1, C2 and F3 are located on a mirror plane. Similar to trifluoromethylsilane **2e**[24] the pentafluoroethyl group is present in a staggered configuration relative to the methyl groups.

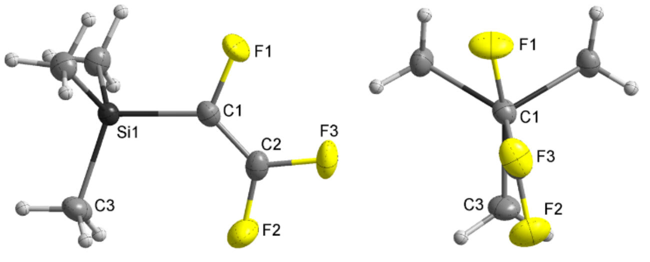


Figure 6. Molecular structure of Si(CH$_3$)$_3$(C$_2$F$_3$) (**2d**) in two different perspectives. Thermal ellipsoids are shown at 50 % probability. Selected bond lengths (pm) and (torsion) angles (°): Si1-C1 188.9(2), Si1-C3 185.7(2), C1-F1 137.3(2), C2-F2 131.9(3), C2-F3 132.5(2), C1-C2 131.2(3), C3-Si1-C1 109.2(1), Si1-C1-C2 131.0(2), C3-Si1-C1-C2 13.1(2), F1-C1-C2-F3 −0.1(3).

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Trifluorovinylsilane **2d** crystallizes in the monoclinic space group *P*2$_1$. In contrast to pentafluoropropenylsilane **2a** atom F1 takes on a nearly staggered configuration to the methyl groups. Most of the structural parameters differ only slightly from those of the gas phase structure, except for the orientation of the trifluorovinyl group. In gas phase the conformation with F1 being syn-periplanar to the carbon atom of one methyl group is favored.[25]

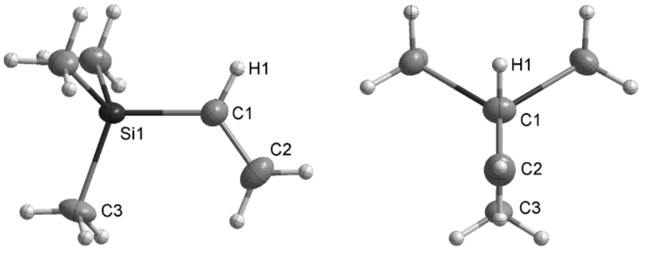

Figure 7. Molecular structure of Si(CH$_3$)$_3$(C$_2$H$_3$) (**2f**) in two different perspectives. Thermal ellipsoids are shown at 50 % probability. Selected bond lengths (pm) and angles (°): Si1-C1 186.49(8), Si1-C3 186.85(9), C1-C2 132.9(1), C3-Si1-C1 109.95(4), Si1-C1-C2 125.54(9).

Vinylsilane **2f** crystallizes in the monoclinic space group *P*2$_1$/*m*. C3, Si1, C1 and C2 are located on the mirror plane. H1 assumes a fully staggered configuration to the methyl groups which leads to a structure similar to the fluorinated analog **2d**.

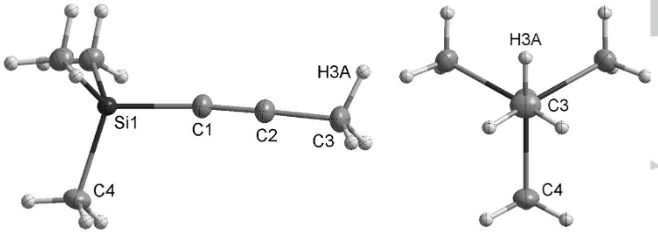

Figure 8. Molecular structure of Si(CH$_3$)$_3$(C$_3$H$_3$) (**2g**) in two different perspectives. Thermal ellipsoids are shown at 50 % probability. Selected bond lengths (pm) and angles (°): Si1-C1 183.52(4), Si1-C4 186.29(4), C1-C2 121.21(5), C2-C3 145.72(6), C4-Si1-C1 107.98(2), Si1-C1-C2 175.53(4), C1-C2-C3 178.57(4).

Propynylsilane **2g** crystallizes in the orthorhombic space group *Pnma*. Contrary to the fluorinated analog **2b** the hydrogen atoms of the propynyl group are present in a staggered disposition to the methyl groups at the silicon atom. C4, Si1, C1 and C3 are located on the mirror plane.

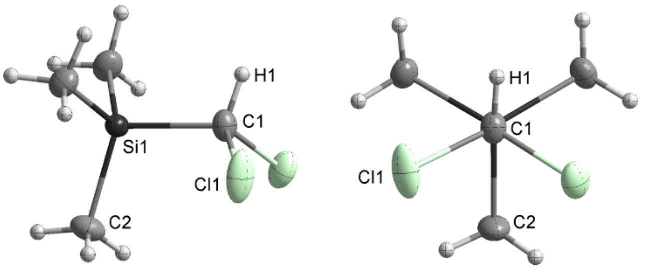

Figure 9. Molecular structure of Si(CH$_3$)$_3$(CCl$_2$H) (**2i**) in two different perspectives. Thermal ellipsoids are shown at 50 % probability. The asymmetric unit contains two molecules of which only one is shown for clarity. Selected bond lengths (pm) and angles (°): Si1-C1 190.5(2), Si1-C2 185.4(2), C1-Cl1 179.1(2), C1-Si1-C2 107.65(8), C2-Si1-C1-Cl1 64.0(1).

Dichloromethylsilane **2i** crystallizes in the orthorhombic space group *P*2$_1$2$_1$2$_1$. The dichloromethyl group takes on a staggered configuration to the methyl groups.

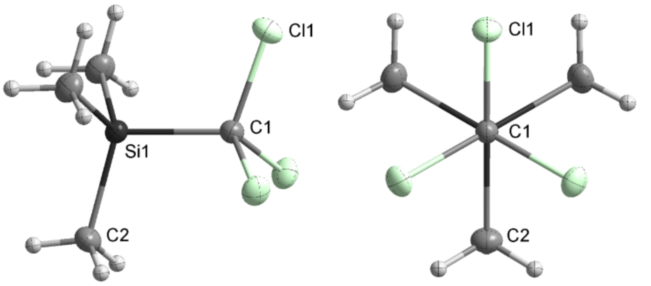

Figure 10. Molecular structure of Si(CH$_3$)$_3$(CCl$_3$) (**2j**) in two different perspectives. Thermal ellipsoids are shown at 50 % probability. The asymmetric unit contains two molecules of which only one is shown for clarity. Selected bond lengths (pm) and angles (°): Si1-C1 193.0(1), Si1-C2 185.5(1), C1-Cl1 178.2(1), C1-Si1-C2 105.92(5).

Trichloromethylsilane **2j** crystallizes in the orthorhombic space group *Pnma*. The trichloromethyl group takes on a fully staggered configuration to the methyl groups. C2, Si1, C1 and Cl1 are located on the mirror plane.

Among the perfluoroorganylsilanes **2a-e** the Si-C bond lengths to the methyl groups are virtually identical whereas the Si-C bond lengths to the perfluoroorganyl groups differ significantly. Pentafluoroethylsilane **2c** features the longest Si-C bond (195.1(2) pm), closely followed by trimethyl(trifluoromethyl)silane (**2e**) with 194.3(12) pm[24]. The next two are **2a** (192.0(1) pm) and **2d** (188.9(2) pm) featuring perfluoroalkenyl substituents. Perfluoropropynylsilane **2b** displays the shortest Si-C bond length (186.5(2) pm). Apparently, the Si-C bond lengths to the perfluoroorganyl groups do not correlate with the strength of the electron withdrawing effect, classified by the C-O bond lengths in Figure 1. Since the bond length decreases from alkyl to alkenyl and alkynyl substituents it is reasonable to assume that it depends on the hybridization of the respective orbitals. An NBO analysis revealed that an increasing s orbital contribution from the involved orbital of the substituent correlates with a shortened Si-C bond (see Table 1). Since alkyl substituent **c** is bulkier than **e** and

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alkenyl **a** bulkier than **d** the steric demand of the attached perfluoroorganyl substituent might also be of interest. The structural parameters of the calculated perfluoroorganyl silanes **2a-e** differ little from those in the solid state and the Si-C bond lengths to the perfluoroorganyl groups display the same tendency. The non-fluorinated silanes **2f-h** each display a shorter Si-C bond than their fluorinated analogs which might arise from the decreased sterical demand of the non-fluorinated substituents. Although the respective orbitals from methyl substituent **h** display the highest p orbital contribution the Si-C bond length in the solid state is slightly shorter than that of vinylsilane **2f**. Silanes **2f** and **2g** follow the same tendency as the fluorinated silanes. Propynylsilane **2g** features the shortest Si-C bond of all examined silanes.

The Si-C bond in trichloromethylsilane **2j** is longer than in dichloromethylsilane **2i** which might simply arise from the size of the substituents with the incompletely chlorinated substituent **i** being less bulky. The calculated Si-C bond of the trichloromethylsilane **2j** is longer than the Si-C bond of the fluorinated analog **2e** in contrast to the experimental values. However, using APFD, which takes dispersion effects into account, instead of B3LYP, the calculated bond length (193.42 pm) is in much better agreement with the experimental value. The same applies to dichloromethylsilane **2i** (191.38 pm). This indicates that dispersion effects influence the Si-C bond length in the case of chlorine-containing substituents.

Table 1. Calculated (B3LYP/6-311++g(3d,p)[16]) and experimental structural characteristics of silanes **2a-j** as well as sp-hybridization of the respective orbitals from the substituents **a-j** involved in the Si-C-bond, determined by NBO analysis[26].

Substituent	d(Si-C)/pm calc.	d(Si-C)/pm exp.	hybridization
C_2F_5 (**c**)	195.93	195.1(2)	sp1.81
CF_3 (**e**)	194.39	194.3(12)[24]	sp1.53
C_3F_5 (**a**)	192.77	192.0(1)	sp1.49
C_2F_3 (**d**)	189.38	188.9(2)	sp1.41
C_3F_3 (**b**)	185.97	186.5(2)	sp0.96
CH_3 (**h**)	188.45	185.0(11) / 185.5(5)[27]	sp2.38
C_2H_3 (**f**)	187.72	186.49(8)	sp1.95
C_3H_3 (**g**)	183.79	183.53(4)	sp1.00
$CHCl_2$ (**i**)	192.41	190.5 (2)	sp1.75
CCl_3 (**j**)	194.70	193.0(1)	sp1.52

Conclusion

Treatment of 2,3,3,3-tetrafluoropropene with two equivalents of *n*-butyllithium leads to the formation of trifluoropropyn-1-yllithium which is a relatively stable transfer agent for the trifluoropropyn-1-yl group. Intermediately formed tetrafluoropropenyllithium on the other hand decays even at −80 °C under elimination of lithium fluoride. The Si-C bond lengths towards the perfluoroorganyl groups **a-e** of silanes **2a-e** correlate nicely with the hybridization of the respective orbitals. A larger p orbital contribution correlates with a longer bond. The non-fluorinated silanes **2f-h** each display a shorter Si-C bond than their fluorinated analogs. Trichloromethylsilane **2j** features a longer Si-C bond than dichloromethylsilane **2i** which was ascribed to the smaller size of the partly chlorinated substituent **i.** The Si-C bond length of trichloromethylsilane **2j** is shorter than the one of silane **2e** which features a less bulky trifluoromethyl substituent. This seems to arise from dispersion effects.

Experimental Section

All chemicals (including vinylsilane **2f** and propynylsilane **2g**) were obtained from commercial sources and used without further purification. *n*-Butyllithium was obtained from a solution in *n*-hexane (1.6 M) by evaporation of the solvent. The amount of *n*-butyllithium was determined by the weight of the solution. Standard high-vacuum techniques were employed throughout all preparative procedures. Non-volatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques. NMR spectra were recorded on a Bruker Model Avance III 300 (^{7}Li 116.6 MHz; ^{19}F 282.4 MHz) spectrometer. Positive shifts are downfield from the external standard CCl_3F (^{19}F). The NMR spectra were recorded in a non-deuterated solvent equipped with a capillary filled with acetone-D_6. All crystals were grown *in situ* inside a capillary filled with the melt by manually generating a crystal seed at temperature $T_{(seed)}$ (**2a-d**, **2f-g**) or cooling slowly along a temperature ramp $T_{(ramp)}$ (**2i-j).** After cooling to the temperature for the measurement $T_{(meas)}$ the crystal data were collected on a Rigaku Supernova diffractometer using Mo-K_α (λ = 0.71073 Å) radiation. Using Olex2[28], the structures were solved with the ShelXT[29] structure solution program using Intrinsic Phasing and refined with the ShelXL[30] refinement package using Least Squares minimisation. (Dichloromethyl)trimethylsilane (**2i**) and Trimethyl(trichloromethyl)silane (**2j**) were prepared according to literature procedures.[31] Further purification was achieved by vacuum distillation with Vigreux column (**2i**) or sublimation (**2j**).

Formation of trifluoropropyn-1-yllithium (1b) – NMR spectroscopic investigation at low temperatures: *n*-Butyllithium (1.6 M in *n*-hexane, 122 mg, 287 µmol) was cooled to −100 °C in a Young NMR tube. Diethyl ether (approx. 0.5 ml) and 2,3,3,3-tetrafluoropropene (6 mbar, 150 µmol) were added by condensation and mixed by shaking. The NMR tube was transferred immediately into the NMR spectrometer which was previously cooled to −80 °C. The sample was gradually warmed to −30 °C and monitored by ^{7}Li and ^{19}F NMR spectroscopy meanwhile. Subsequently it was warmed to room temperature.

Stability of trifluoropropyn-1-yllithium (1b) at room temperature: 2,3,3,3-tetrafluoropropene (1.75 mmol) was added to a solution of *n*-butyllithium (1.6 M in *n*-hexane, 1.42 g, 3.34 mmol) in diethyl ether (20 ml) at −60 °C. During 3 h it was gently warmed to room temperature. Afterwards chlorotrimethylsilane (277 mg, 2.55 mmol) was added to the colorless solution. Hexafluorobenzene (77 mg, 414 mmol) was added as reference and the conversion rate was determined via ^{19}F NMR spectroscopy. Trimethyl(trifluoropropyn-1-yl)silane (1.64 mmol, 98 % based on *n*-butyllithium) was detected.

Synthesis of (E)-trimethyl(pentafluoropropen-1-yl)silane (2a): (Z)-1,2,3,3,3-pentafluoroprop-1-ene (17.6 mmol) was added to a solution of *n*-butyllithium (16.0 mmol) in dimethyl ether (50 ml) at −80 °C. After 20 min chlorotrimethylsilane (1.56 g, 14.4 mmol) was added to the brown solution. It was gently warmed to room temperature whereby the solvent vaporized and a solid precipitated. After condensation of all volatile compounds (*E*)-trimethyl(pentafluoropropen-1-yl)silane (1.86 g, 9.14 mmol, 63 %) was obtained as a pale yellow liquid. NMR data[21] as in the literature.

Synthesis of trimethyl(trifluoropropyn-1-yl)silane (2b): 2,3,3,3-Tetrafluoroprop-1-ene (42 mmol) was added to a solution of *n*-butyllithium

(76 mmol) in dimethyl ether (approx. 100 ml) at −80 °C. During 2 h it was gently warmed towards −40 °C and after that period of time chlorotrimethylsilane (2.98 g, 27.4 mmol) was added and the mixture was gently warmed towards room temperature whereby the solvent vaporized and a solid precipitated. The suspension turned black. Trimethyl(trifluoropropyn-1-yl)silane (3.24 g, 19.5 mmol, 71 %) was purified by fractional condensation (–80 °C, 10^{-3} mbar) and obtained as a colorless liquid. NMR data[32] as in the literature.

Synthesis of trimethyl(pentafluoroethyl)silane (2c): Pentafluoroethane (18 mmol) was added to a solution of *n*-butyllithium (16.3 mmol) in dimethyl ether (approx. 50 ml) at −80 °C. After 30 min chlorotrimethylsilane (1.52 g, 14.0 mmol) was added to the slightly pink solution. It was gently warmed to room temperature whereby the solvent vaporized and a colorless solid precipitated. Trimethyl(pentafluoroethyl)silane (1.88 g, 9.78 mmol, 70 %) was purified by fractional condensation (–84 °C, 10^{-3} mbar) and obtained as a colorless liquid. NMR data[23] as in the literature.

Synthesis of trimethyl(trifluorovinyl)silane (2d): 1,1,1,2-Tetrafluoroethane (25 mmol) was added to a solution of *n*-butyllithium (49.0 mmol) in dimethyl ether (approx. 100 ml) at −80 °C. After 45 min chlorotrimethylsilane (2.22 g, 20.5 mmol) was added to the colorless solution. It was gently warmed to room temperature whereby the solvent vaporized and a solid precipitated. The suspension turned brown. Trimethyl(trifluorovinyl)silane (1.79 g, 11.6 mmol, 57 %) was purified by fractional condensation (–84 °C, 10^{-3} mbar) and obtained as a colorless liquid. NMR data[33] as in the literature.

Table 2. Crystal data and refinement characteristics for silanes **2a**-**j**.

	$Si(CH_3)_3(C_3F_5)$ (**2a**)	$Si(CH_3)_3(C_3F_3)$ (**2b**)	$Si(CH_3)_3(C_2F_5)$ (**2c**)	$Si(CH_3)_3(C_2F_3)$ (**2d**)[a]	$Si(CH_3)_3(C_2H_3)$ (**2f**)[b]	$Si(CH_3)_3(C_3H_3)$ (**2g**)	$Si(CH_3)_3(CCl_2H)$ (**2i**)[c]	$Si(CH_3)_3(CCl_3)$ (**2j**)[d]
CCDC	2041674	2041670	2041671	2041668	2041669	2041675	2041673 _B	2041672
$T_{(seed)}$ resp $T_{(ramp)}$ /K	180.4	200.3	218.4	152.8	140.4	203.6	260 - 255	315 - 290
Empirical formula	$C_6H_9F_5Si$	$C_6H_9F_3Si$	$C_5H_9F_5Si$	$C_5H_9F_3Si$	$C_5H_{12}Si$	$C_6H_{12}Si$	$C_4H_{10}Cl_2Si$	$C_4H_9Cl_3Si$
M /g·mol^{-1}	204.22	166.22	192.21	154.21	100.24	112.25	157.11	191.55
$T_{(meas)}$ /K	94.0(1)	100.0(1)	94.0(1)	94.0(1)	95.0(1)	95.0(1)	95.0(1)	95.0(1)
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$P\text{-}1$	$P2_1/m$	$Cmc2_1$	$P2_1$	$P2_1/m$	$Pnma$	$P2_12_12_1$	$Pnma$
a /pm	8.24807(13)	5.9441(4)	9.70677(13)	5.9571(7)	6.2998(2)	10.77321(13)	6.85030(10)	11.8194(5)
b /pm	11.32672(19)	9.3290(6)	8.08636(10)	11.1094(10)	7.5490(2)	7.74259(10)	10.6113(2)	10.5592(4)
c /pm	16.0163(2)	8.0412(4)	10.96549(17)	6.3622(8)	7.6208(3)	9.26001(12)	22.0895(4)	6.8560(3)
α /°	75.9620(14)	90	90	90	90	90	90	90
β /°	75.5766(13)	99.388(5)	90	111.284(14)	96.625(3)	90	90	90
γ /°	80.7616(14)	90	90	90	90	90	90	90
V /(10^6·pm^3)	1397.86(4)	439.93(4)	860.71(2)	392.33(8)	360.01(2)	772.401(17)	1605.70(5)	855.65(6)
Z	6	2	4	2	2	4	8	4
ρ_{calc} /g·cm^{-3}	1.456	1.255	1.483	1.305	0.925	0.965	1.3	1.487
μ /mm^{-1}	0.276	0.245	0.293	0.269	0.208	0.2	0.856	1.12
F(000)	624	172	392	160	112	248	656	392
Crystal size /mm^3	0.595 × 0.267 × 0.244	0.621 × 0.449 × 0.437	0.586 × 0.226 × 0.2	0.6 × 0.267 × 0.262	0.66 × 0.329 × 0.252	0.597 × 0.334 × 0.328	0.598 × 0.326 × 0.275	0.606 × 0.288 × 0.279
Radiation /Å	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)
2Θ range for data collection /°	3.728 to 64.568	5.134 to 60.064	6.558 to 72.636	7.336 to 64.232	5.382 to 78.89	5.802 to 118.604	6.226 to 74.098	6.87 to 73.952
Index ranges	$-12 \le h \le 12$ $-16 \le k \le 16$ $-23 \le l \le 23$	$-8 \le h \le 8$ $-13 \le k \le 13$ $-11 \le l \le 11$	$-16 \le h \le 16$ $-13 \le k \le 13$ $-18 \le l \le 18$	$-8 \le h \le 8$ $-16 \le k \le 16$ $-9 \le l \le 9$	$-11 \le h \le 9$ $-13 \le k \le 13$ $-13 \le l \le 13$	$-26 \le h \le 26$ $-18 \le k \le 18$ $-22 \le l \le 22$	$-11 \le h \le 11$ $-17 \le k \le 17$ $-37 \le l \le 36$	$-19 \le h \le 19$ $-17 \le k \le 17$ $-11 \le l \le 11$
Total data collected	69019	25318	29412	8435	41155	89667	50811	29532
Unique data	9318 [R_{int} = 0.0271, R_{sigma} = 0.0164]	1363 [R_{int} = 0.0777, R_{sigma} = 0.0213]	2176 [R_{int} = 0.0296, R_{sigma} = 0.0119]	2600 [R_{int} = 0.0194, R_{sigma} = 0.0367]	4753 [R_{int} = 0.0385, R_{sigma} = 0.0711]	5945 [R_{int} = 0.0407, R_{sigma} = 0.0140]	7868 [R_{int} = 0.0357, R_{sigma} = 0.0230]	2200 [R_{int} = 0.0519, R_{sigma} = 0.0198]
Observed data [$I > 2\sigma(I)$]	8150	1230	2151	2399	3986	4624	7210	1958
Data / restraints / parameters	9318 / 0 / 433	1363 / 0 / 74	2176 / 1 / 77	2600 / 1 / 119	4753 / 0 / 64	5945 / 0 / 66	7868 / 0 / 208	2200 / 0 / 62
Goodness of fit on F^2	1.03	1.145	1.033	1.083	0.976	1.057	1.072	1.068

R_1 / wR_2 [$I > 2\sigma(I)$]	0.0308 / 0.0772	0.0463 / 0.1215	0.0239 / 0.0672	0.0294 / 0.0746	0.0325 / 0.0836	0.0292 / 0.0953	0.0279 / 0.0577	0.0253 / 0.0572
R_1 / wR_2 [all data]	0.0368 / 0.0807	0.0510 / 0.1253	0.0241 / 0.0673	0.0324 / 0.0757	0.0398 / 0.0857	0.0412 / 0.1024	0.0328 / 0.0595	0.0303 / 0.0594
$\Delta\rho_{max/min}$ /e·Å^{-3}	0.38 / -0.28	0.63 / -0.40	0.34 / -0.27	0.31 / -0.30	0.52 / -0.25	0.78 / -0.19	0.39 / -0.37	0.47 / -0.44
Flack parameter			0.00(2)	-0.09(10)			0.21(5)	

[a] The crystal was twinned (ratio 54:46), component 2 rotated by 180.0° around [-0.67 -0.00 0.74] (reciprocal) or [-0.71 -0.00 0.71] (direct). [b]. Three crystal domains with an approximate ratio of 2:1:1 were indexed and taken into account for data integration. For structure refinement only the main domain and composite reflections were used. [c] Refined as inversion twin with a ratio of 79:21. [d] The crystal undergoes a phase transition at ca. 265 K, leading to oligo-crystalline material. Even so, it was possible to index and integrate the diffraction pattern of a single domain, the other ones were neglected.

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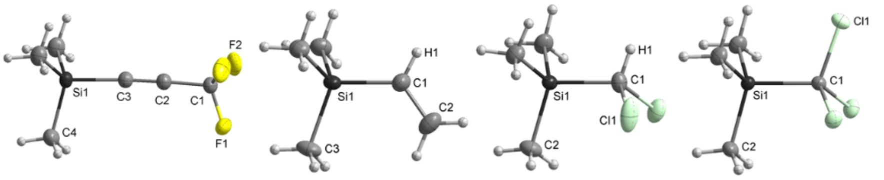

Trimethylsilanes Si(CH_3)$_3$X with different substituents X have been structurally characterized. The lengths of the bonds between the silicon and the carbon atoms of X correlate with the hybridization of the respective orbitals and the sterically demand of X. Furthermore, a route for generating trifluoropropyn-1-yllithium from the cryogen 2,3,3,3-tetrafluoropropene (HFO-1234yf) and *n*-butyllithium is described.