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Highly reactive oligosilyltriflates—synthesis, structure and rearrangement†

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The novel branched oligosilyltriflates of formula $[TfO(Me_3Si)_2Si]_2E$ (**2a–d**) [E = 0 (**2a**), $SiMe_2$ (**2b**), $GeMe_2$ (**2c**), $SiMe_2$–$SiMe_2$ (**2d**)] and $[TfO(Me_3Si)_2SiSiMe_2]_3SiMe$ (**9**) have been prepared by the protodesilylation of $[Ph(Me_3Si)_2Si]_2E$ (**1a–c**), $[H(Me_3Si)_2Si]_2E$ (**5d**) and $[Ph(Me_3Si)_2SiSiMe_2]_3SiMe$ (**8**) using TfOH (CF_3SO_3H) as reagent in almost quantitative yields. The crystal structure of **2b** is reported.

Introduction

In recent years there has been a growing interest in well-defined polyfunctionalized oligosilanes as sources of materials with novel electronic properties.[1] The development of such compounds requires new synthetic methods for the manipulation of functional groups on the silicon backbone without Si–Si bond cleavage. One of such useful groups is the trifluoromethanesulfonate group (TfO = CF_3SO_3), which can be selectively introduced by protodesilylation of hydrido, vinyl, allyl and phenyl silanes with trifluoromethanesulfonic acid (TfOH) giving the desired silyltriflates in high yields.[2]

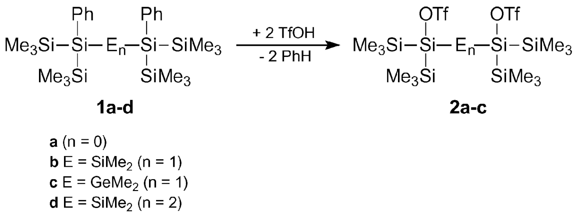
Although the formation of multiple triflate functionalized oligosilanes, often obtained as thermally unstable oils, has been reported by protodesilylation of mainly perphenylated linear,[3] cyclic[4] and dendrimeric oligosilanes,[5] nothing is known about their structures in the solid state. Herein we wish to report a rather straightforward and selective synthesis of a series of novel isolable and crystalline permethylated oligosilanes with two or three triflate functionalities and we report the first crystal structure of an oligosilylbis(triflate).

Results and discussion

Phenylsilanes, readily available and reactive derivatives towards the protodesilylation reaction, are ideal starting materials for the synthesis of oligosilyl triflates. Disadvantageous, however, is that in the presence of TfOH or related electrophilic reagents, linear oligosilanes with more electropositive substituents such as alkyl or silyl tend to rearrange under Si–Si bond cleavage or migration of substituents to branched structures.[6] To avoid such unpredictable skeletal rearrangements, we primarily focused on the synthesis of already branched oligosilanes in which both phenyl groups, connected to tertiary silicon atoms, are separated from each other by different spacers groups.

The corresponding diphenyloligosilanes **1a–d** (supporting information†) have been synthesized in good yields *via* salt metathesis reactions by treatment of phenylbis(trimethylsilyl)silylpotassium with $BrCH_2CH_2Br$, Cl_2SiMe_2, Cl_2GeMe_2 and $ClMe_2SiSiMe_2Cl$, respectively.[7] For the protodesilylation of **1a–d**, the progress of the reaction was monitored by ^{29}Si- and ^{19}F-NMR spectroscopy.

When the oligosilanes **1a–c** were allowed to react with two equivalents of TfOH, immediately new fluorine signals for the triflate group appeared at around −75 ppm in the ^{19}F NMR spectrum and a significant shift for the tertiary silicon atom to lower field was observed: −70.9 (**1a**), −70.5 (**1b**) and −62.8 ppm (**1c**) to 40.8 (**2a**), 39.3 (**2b**) and 44.8 ppm (**2c**).[8] The remarkable changes in the chemical shift clearly indicate a complete Si–Ph bond cleavage under formation of the corresponding SiOTf functionality. The reaction proceeds facilely and highly selectively yielding the oligosilylbis(triflates) **2a–c** in almost quantitative yields after removal of the solvent (eqn (1). The triflates so obtained are surprisingly thermally stable but highly moisture sensitive, colourless solids. They can be further purified by crystallization from pentane at low temperatures. The NMR spectra of the crystalline compounds are rather straightforward and are in full agreement with the structures proposed.



(1)

In addition, the molecular structure of **2b** has been confirmed by X-ray crystallography. Suitable crystals were grown from pentane solutions at RT. As seen in Fig. 1, the molecule has a total of 7 silicon atoms and a longest chain of 5 silicon atoms bearing two triflate groups at the 2- and 4-positions. Most of Si–Si bond lengths lie unremarkably within the range of 2.36–2.38 Å and the Si–Si–Si bond angles are variable but generally within the range 110–119°.

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† Electronic supplementary information (ESI) available: experimental details. See DOI: 10.1039/b408573f

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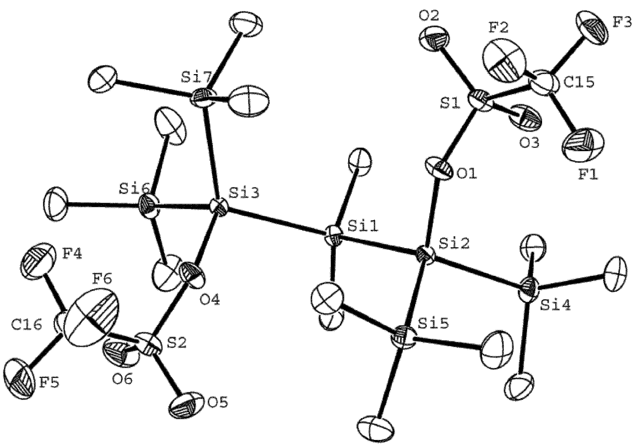
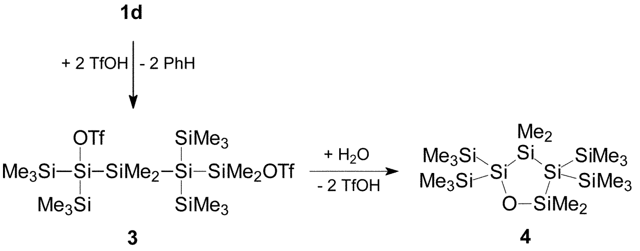


Fig. 1 Molecular structure of **2b** in the crystal. The thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si_2–O_1 1.778(2), Si_3–O_4 1.780(2), S_1–O_1 1.520(2), S_2–O_4 1.494(3), Si_1–Si_2 2.3581(14), Si_1–Si_3 2.3582(14), Si_3–Si_6 2.3785(14), Si_2–Si_4 2.3821(15), S_1–O_1–Si_2 132.2(2), S_2–O_4–Si_3 137.1(2), Si_2–Si_1–Si_3 118.90(5), Si_1–Si_2–Si_5 118.22(5), Si_1–Si_2–Si_4 109.90(5), Si_1–Si_3–Si_7 116.45(5), Si_1–Si_3–Si_6 109.80(5).

The Si_4–Si_2–Si_1–Si_3–Si_6 pentasilane chain approximately adopts an all-*trans* conformation (T-T-T),[9] which is known to be optimal for σ-conjugation.[10] The geometry around the silicon atoms Si_2 and Si_3 attached to the triflate groups can be described as distorted tetrahedral. As a result of steric strain in the molecule the angles S_1–O_1–Si_2 [132.2°] and S_2–O_4–Si_3 [137.1°] are larger then in Ph_3SiOTf [11] with 129.06° but smaller than in $(Bu^t)_3SiOTf$ [12] in which the bulky tertiary butyl groups force a significant widening of the angle to a value of 149.3°. The length of the Si–O bonds in **2b**, 1.778 Å and 1.78 Å, is not only significantly longer than those normally observed for Si–O bonds [1.64–1.66 Å],[13] it is also longer than in $(Bu^t)_3SiOTf$ [1.742 Å] and in Ph_3SiOTf [1.743 Å], implying that there is a significant ionic component in the bonding.[14]

Moreover, it is the longest so far observed for tetrahedral silyltriflates,[15] reflecting the strong electronic influence of the surrounding electropositive silyl substituents, which act as more electron donating groups than their carbon analogues in $(Bu^t)_3SiOTf$. The silylium cation character in this compound is also reflected in the sum of the three Si–Si–Si bond angles (338.5° and 336.8°) around the two silyltriflate functionalities indicating a substantial flattening of the oligosilane backbone.

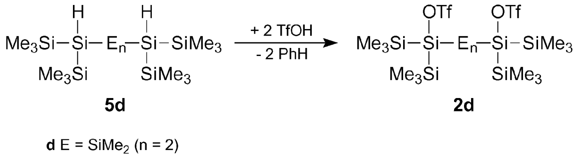
In striking contrast to the protodesilylation reactions described above, treatment of **1d** with TfOH in dichloromethane yields a product which exhibits four signals in the ^{1}H-NMR spectrum, two for a $SiMe_3$ and two for a $SiMe_2$ group, instead of the two signals expected for bis(triflate) **2d**. However, the structure of the liquid compound was clearly identified by means of NMR spectroscopy as the rearranged oligsilyl(bis)-triflate **3**, which shows 6 signals in the ^{29}Si-NMR spectrum, two for a silyltriflate group, two for a primary silicon, one for a quaternary and one for a secondary silicon as well (Scheme 1). In addition, the proposed structure of **3** could be confirmed by hydrolysis, which gave the cyclic siloxane **4** exclusively (supporting information†).



Scheme 1 Reaction of **1d** with TfOH.

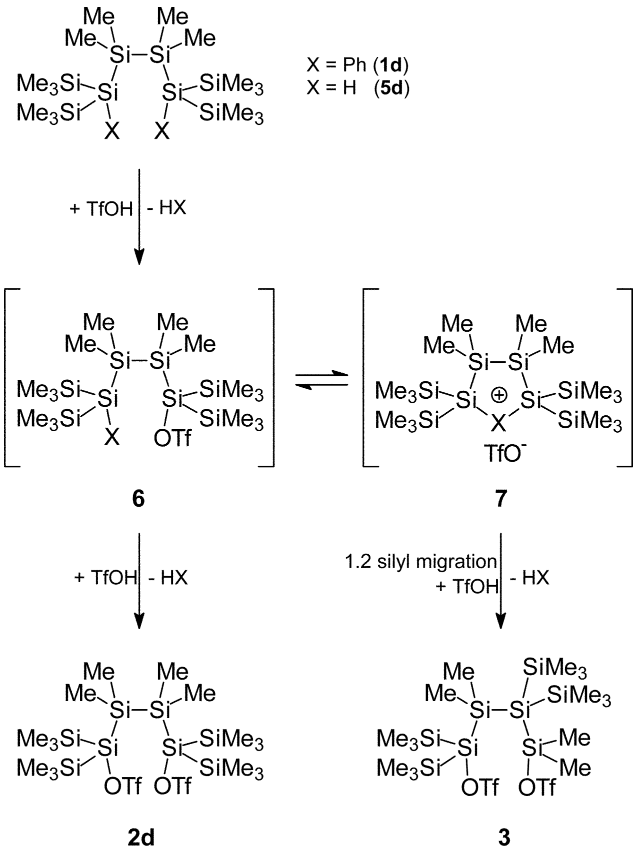
The formation of **3** can be rationalized as a 1,2-oligosilyl rearrangement in the oligosilane backbone reflecting clearly the tendency of oligosilanes to undergo skeletal rearrangements under formation of highly branched structures as already could be shown by Ishikawa *et al.*[6a] Attempts to avoid such a rearrangement by using the less polar solvent pentane led only to mixtures of **3** and the bis(triflate) **2d**, which could not be separated.

However, the reaction of the dihydrido compound **5d** with TfOH gave the desired bis(triflate) **2d** in almost quantitative yields according to the NMR spectra (eqn (2)). To our surprise, **2d** a stable crystalline solid does not tend to undergo a skeletal rearrangement into **3**, which, is in sharp contrast to the reaction of **1d** with TfOH.

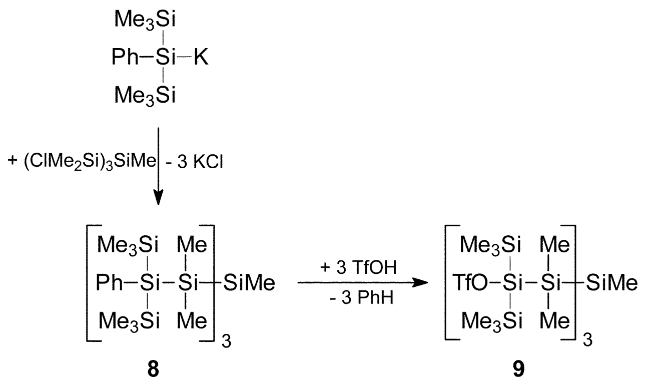


(2)

The remarkable difference in the selectivity of the protodesilylation reaction of **1d** compared to **5d**, may be attributed to an intramolecular donor–acceptor interaction of the silyltriflate with the phenyl group. This may result in the transient formation of the bridged carbocationic species **7** after the first protodesilylation step (Scheme 2). Similar 1,5-bridged cationic systems with a thermodynamically more stable carbosilane backbone have already been characterized by NMR spectroscopy and are supported by quantum-mechanical calculations,[16] and 1,3-bridged cationic carbosilanes are supposed to be intermediates in the solvolysis of silicon halides with the $[(Me_2ArSi)(Me_3Si)_2C]$ group.[17] A hydrido group (X = H) being only a weak donor should not interact intramolecularly with the silyltriflate, thereby a rapid second protodesilylation occurs without a competitive skeletal rearrangement.



Scheme 2 Proposed mechanism for the skeletal rearrangement.



Scheme 3 Synthesis of triflate **9**.

To summarise, the strong π-donor interaction of the phenyl group does not only significantly stabilize the transient bridged species **7**, but leads to an increased reaction rate of the intramolecular 1.2-oligosilyl migration by anchimeric assistance.

Finally, and with the intention of confirming the concept successfully applied for the triflates **2a–c** mentioned above, we extended our studies to the synthesis of triflate functionalized dendritic oligosilanes. As substrate we used compound **8**, an oligosilane dendrimer of first generation with a longest chain of 7 silicon atoms, which was prepared analogously by reaction of three equiv. of Ph(Me$_3$Si)Si–K with (ClMe$_2$Si)$_3$SiMe in good yields (Scheme 3).

Whereas, the treatment of **8** with three equiv. of TfOH in dichloromethane gave a mixture of several rearranged products of unknown composition, a microcrystalline precipitate of the dendritic oligosilyltris(triflate) **9** was formed using pentane as solvent. Although we were not able to obtain single crystals of **9** suitable for X-ray diffraction studies, the structure proposed was unambiguously evidenced by means of elemental analysis and NMR spectroscopic data.

Conclusion

The branched oligosilyltriflates **2a–d** and **9** have been prepared by protodesilylation using TfOH as reagent. Although highly moisture sensitive, these oligosilyltriflates are thermally stable and easy to handle crystalline compounds which can be obtained even in larger amounts. Therefore, they might be of interest as Lewis acid catalysts for a variety of organic transformations and as reactive reagents for the protection of OH groups in sugars or other natural products. Investigations with regard to the latter are currently in progress.

Experimental

General remarks

All reactions involving organometallic reagents were carried out under an atmosphere of argon using standard Schlenk techniques. TfOH (CF$_3$SO$_3$H) was distilled prior to use, Ph(Me$_3$Si)$_2$Si-K × 3 THF,[18] (Me$_3$Si)$_2$SiPh–SiPh(SiMe$_3$)$_2$, (**1a**),[19] and (Me$_3$Si)$_2$SiH–SiMe$_2$–SiMe$_2$–SiH(SiMe$_3$)$_2$, (**5d**),[20] were prepared as previously described. The full preparation and characterization of the oligosilanes **1b-d**, **4** and **8** is given in the supporting information†.

General procedure for the protodesilylation of 1a–d, 5d and 8. In a typical experiment, TfOH (1.1 equiv.) was added to a stirred solution of **1a–d**, **5d** or **8** in pentane or CH$_2$Cl$_2$ at 0 °C. The mixture was allowed to warm up to RT within 2 h. After evaporation of the solvent the solid residue was dried under high vacuum to remove the excess TfOH. Analytically pure samples of **2a–d** and **9** were obtained by recrystallization from pentane at −40 °C.

1,1,1,4,4,4-Hexamethyl-2,3-bis(trifluoromethanesulfonato)-2,3-bis(trimethylsilyl)tetrasilane (2a). 1a (1.355 g, 2.7 mmol), TfOH (0.5 ml, 5.7 mmol) and pentane (10 ml). Yield 1.36 g (78%); ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ 0.33 (s, SiMe$_3$, 36H); ^{13}C NMR (C$_6$D$_6$, 63 MHz): δ 0.0 (SiMe$_3$), 119.0 (q, $^1J_{\mathrm{C-F}}$ = 318.1 Hz, CF$_3$); ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −8.7 (SiMe$_3$), 40.8 (SiOTf); ^{19}F NMR (C$_6$D$_6$, 235.3 MHz): δ −74.4 (CF$_3$); Anal. Calc. for C$_{14}$H$_{36}$F$_6$O$_6$S$_2$Si$_6$ (647.05): C, 25.99; H, 5.61. Found: C, 25.67; H, 5.65%.

1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trifluoromethanesulfonato)-2,4-bis(trimethylsilyl)pentasilane (2b). 1b (1.51 g, 2.7 mmol), TfOH (0.5 ml, 5.7 mmol) and CH$_2$Cl$_2$ (*ca.* 10 ml). Yield 1.69 g (89%); ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ 0.31 (s, SiMe$_3$, 36H), 0.44 (s, SiMe$_2$, 6H); ^{13}C NMR (C$_6$D$_6$, 63 MHz): δ 0.1 (SiMe$_3$), −2.7 (SiMe$_2$), 119.1 (q, $^1J_{\mathrm{C-F}}$ = 318.5 Hz, CF$_3$); ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −10.0 (SiMe$_3$), −32.4 (SiMe$_2$), 39.3 (SiOTf); ^{19}F NMR (C$_6$D$_6$, 235.3 MHz): δ −74.4 (CF$_3$); Anal. Calc. for C$_{16}$H$_{42}$F$_6$O$_6$S$_2$Si$_7$ (705.21): C, 27.25; H, 6.00. Found: C, 26.34; H, 6.30%.

1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trifluoromethanesulfonato)-2,4-bis(trimethylsilyl)-3-germa-pentasilane (2c). 1c (1.635 g, 2.7 mmol), TfOH (0.5 ml, 5.7 mmol) and CH$_2$Cl$_2$ (*ca.* 10 ml). Yield 1.84 g (91%); ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ 0.30 (s, SiMe$_3$, 36H), 0.60 (s, GeMe$_2$, 6H); ^{13}C NMR (C$_6$D$_6$, 63 MHz): δ −0.2 (SiMe$_3$), −2.1 (GeMe$_2$), 119.1 (q, $^1J_{\mathrm{C-F}}$ = 317.1 Hz, CF$_3$); ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −9.5 (SiMe$_3$), 44.8 (SiOTf); ^{19}F NMR (C$_6$D$_6$, 235.3 MHz): δ −75.7 (CF$_3$); Anal. Calc. for C$_{16}$H$_{42}$F$_6$O$_6$S$_2$Si$_6$Ge (749.71): C, 25.63; H, 5.65; F, 15.20. Found: C, 25.03; H, 5.34; F, 14.93%.

1,1,1,3,3,4,4,6,6,6-Decamethyl-2,5-bis(trifluoromethanesulfonato)-2,5-bis(trimethylsilyl)hexasilane (2d). 5d (0.40 g, 0.86 mmol), TfOH (0.16 ml, 1.89 mmol) and pentane (*ca.* 5 ml). Yield 0.55 g (84%); ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ 0.27 (s, SiMe$_3$, 36H), 0.50 (s, SiMe$_2$, 12H); ^{13}C NMR (C$_6$D$_6$, 75 MHz): δ 0.0 (SiMe$_3$), −3.0 (SiMe$_2$), 119.1 (q, $^1J_{\mathrm{C-F}}$ = 318.1 Hz, CF$_3$); ^{29}Si NMR (C$_6$D$_6$, 59.6 MHz): δ–32.8 (SiMe$_2$), −10.7 (SiMe$_3$), 42.1 (SiOTf); ^{19}F NMR (C$_6$D$_6$, 235.3 MHz): δ −74.7 (CF$_3$); Anal. Calc. for C$_{18}$H$_{48}$F$_6$O$_6$S$_2$Si$_8$ (763.36): C, 28.32; H, 6.34. Found: C, 27.91; H, 6.22%.

1,1,1,3,3,5,5-Heptamethyl-2,5-bis(trifluoromethanesulfonato)-2,4,4-tris(trimethylsilyl)pentasilane (3). 1d (1.67 g, 2.7 mmol), TfOH (0.5 ml, 5.7 mmol) and CH$_2$Cl$_2$ (*ca.* 10 ml). Yield 1.98 g (96%); ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ 0.27, 0.29 (2s, SiMe$_3$, 2×18H), 0.47, 0.71 (2s, SiMe$_2$, 2×6H); ^{13}C NMR (C$_6$D$_6$, 63 MHz): δ 0.6, 1.4 (SiMe$_3$), 2.8 (SiMe$_2$), 119.1 (q, $^1J_{\mathrm{C-F}}$ = 320.4 Hz, CF$_3$); ^{29}Si NMR (C$_6$D$_6$, 59.6 MHz): δ −10.0, −9.3 (SiMe$_3$), −29.4 (SiMe$_2$), 55.9 (SiMe$_2$OTf), 43.3 (SiOTf), −122.5 (quart. Si); ^{19}F NMR (C$_6$D$_6$, 235.3 MHz): δ −75.5, −74.1 (CF$_3$); Anal. Calc. for C$_{18}$H$_{48}$F$_6$O$_6$S$_2$Si$_8$ (763.36): C, 28.32; H, 6.34. Found: C, 27.78; H, 6.29%.

1,1,1,3,3,4,5,5,7,7,7-Undecamethyl-2,6-trifluoromethanesulfonato-2,6-bis(trimethylsilyl)-4-[1,1,3,3,3-pentamethyl-2-trifluoromethanesulfonato-2-trimethylsilyltrisilanyl]heptasilane (9). 8 (1.75 g, 1.8 mmol), TfOH (0.5 ml, 5.7 mmol) and pentane (*ca.* 10 ml). After a few minutes a white solid immediately precipitates out which was isolated by filtration and drying under vacuum to give pure **9** (1.3 g, 61%); ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ 0.34 (s, SiMe$_3$, 54H), 0.63 (s, SiMe$_2$, 18H) 0.8 (s, SiMe, 3H); ^{13}C NMR (C$_6$D$_6$, 63 MHz): δ 0.5 (SiMe$_3$), 0.2

(SiMe$_2$), 0.8 (SiMe), 127.0 (CF$_3$); ^{19}F NMR (C$_6$D$_6$, 235.3 MHz): δ −74.1 (CF$_3$); Anal. Calc. for $C_{28}H_{75}F_9O_9S_3Si_{13}$ (1188.17): C, 28.30; H, 6.36. Found: C, 28.01; H, 6.13%.

X-ray crystallography

The data collection for **2b** was done on a STOE-IPDS diffractometer using a graphite monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXS-86) and refined by the full matrix least-squares method against F^2 (SHELXL-93)[21] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in theoretical positions and refined using the riding model.

Crystal data. $C_{16}H_{42}F_6O_6S_2Si_7$, $M = 705.25$, colourless prism, monoclinic, space group $P2_1/c$, $a = 8.992(2)$, $b = 16.534(3)$, $c = 23.992(5)$ Å, $\beta = 92.85(3)°$, $V = 3562.6(13)$ Å^3, $T = 200$ K, $Z = 4$, μ(Mo-Kα) = 0.443 mm^{-1}, 8670 reflections measured, 4657 reflections independent of symmetry, 3692 reflections observed [$I > 2\sigma(I)$], 334 parameters, $R1 = 0.045$, w$R2$ (all data) = 0.121.‡

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