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Synthesis, Reactivity and X-Ray Crystal Structure of Tris(pentafluorophenyl)silanol $(C_6F_5)_3SiOH$

This paper is dedicated to the Memory of Professor Renato Ugo, an unforgettable teacher in science and life.

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Abstract. Tris(pentafluorophenyl)silanol $(C_6F_5)_3SiOH$ was prepared from the corresponding chlorosilane $(C_6F_5)_3SiCl$ by an unconventional controlled hydrolysis. The X-ray structure and the reactivity of the new silanol with various bases, with triflic acid and with some rhenium carbonyl complexes are reported. The Si-C_6F_5 bond is easily cleaved in the presence of even weak bases and this behaviour prevented the isolation of the $(C_6F_5)_3SiO^-$ anion and the synthesis of the $[Re(CO)_5COSiR_3]$ derivative. In particular, when $(C_6F_5)_3SiOH$ was reacted with butyllithium and $Re(CO)_5OSO_2CF_3$ the formation of $[Re(CO)_5C_6F_5]$ was observed.

Keywords. Tris(pentafluorophenyl)silanol, fluorinated silanols, rhenium(I) pentacarbonyl complexes, crystal structure.

1. Introduction

The investigation on the structure and reactivity of silica-anchored organometallic species has been improved in the last two decades also through the complementary investigation on the synthesis, structure and reactivity of molecular models bearing silanolate ligands which mimic the silanol groups of the silica surface [1–7]. For instance, some of us reported evidence for the peculiar stabilization of the rhenium pentacarbonyl species $[Re(CO)_5OSi\equiv]$ on the silica surface, but the synthesis of its molecular model $[Re(CO)_5OSiR_3]$ was hampered by the fact that nucleophiles, such as Me_3SiO^-, are exceptionally good *cis*-labilizing ligands that facilitate the instantaneous loss of carbonyl ligands and further nucleophilic attacks to give dimeric units bridged by silanolate groups such as $[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^-$ [8]. The use of a silanolate anion with much lower nucleophilicity, such as the silsesquioxane derivative $(c\text{-}C_6H_{11})_7Si_8O_{12}O^-$, enabled some of us to synthesize and spectroscopically characterize the surface model species $[Re(CO)_5OR]$ $(R=(c\text{-}C_6H_{11})_7Si_8O_{12})$, stable only under CO atmosphere and at 273 K [9]. In order to obtain a different ligand characterized by a similar very poor nucleophilicity, suitable to afford a stable $[Re(CO)_5OSiR_3]$ species by reaction with rhenium pentacarbonyl complexes, we investigated the synthesis and reactivity of $(C_6F_5)_3SiOH$. To our knowledge in the literature $(C_6F_5)_3SiOH$ has been previously briefly mentioned in a communication on the reactivity of $(C_6F_5)_3SiCl$ with water [10], and in a patent for the preparation of polyene compounds obtained in the presence of siloxy-vanadium catalysts of general formula $(R_3SiO)_m(OR')_nVO$ (R = phenyl with one or more electron-withdrawing substituents; R' = alkyl, cycloalkyl, Ph, Ph$_3$Si, etc.; m = 1-3; n

= 3-m) [11], but in both cases, no details about the synthesis and structural characterization were provided.

In this paper, we report the synthesis of $(C_6F_5)_3SiOH$, achieved by a controlled and unusual method of hydrolysis of the corresponding chlorosilane $(C_6F_5)_3SiCl$, together with its X-ray structural characterization and its reactivity with bases, acids and various rhenium carbonyl complexes.

2. Experimental Section

$(C_6F_5)_3SiCl$ was prepared as described in the literature by reacting $(C_6F_5)_3SiPh$ with $AlCl_3$ [12]. $Re(CO)_3(PPh_3)_2CH_3$ [13], $Re(CO)_3(Ph_2PCH_2CH_2PPh_2)CH_3$ [13] and $[Re(CO)_5O_3SCF_3]$ [14] were prepared according to the literature.

Proton sponge (1,8-Bis(dimethylamino)naphthalene, DMAN), triflic acid, benzaldehyde and pyrrolidine were purchased from Sigma Aldrich and used as received. NEt_3 was distilled before use. BuLi (1.6 M in hexane) was purchased from Aldrich in Sure/Seal^{TM} bottles and used under a nitrogen atmosphere. CH_2Cl_2 and toluene were distilled over P_2O_5 and sodium/benzophenone, respectively. $CDCl_3$ and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories, Inc. in 0.75 mL sealed vials and used right after opening.

The products were characterized by ^1H, ^{13}C, ^{19}F, ^{29}Si NMR (Bruker Avance DRX 300 and DRX 400 spectrometers). For ABB'CC' fluorine spin systems the apparent J coupling constants as read on the ^{19}F NMR spectrum are reported. Infrared spectra were collected on Jasco FT IR-420 and Bruker–Vector 22 spectrometers. Elemental analyses were carried out with a Perkin-Elmer CHN 2400 instrument at the Microanalytical Laboratory of the Department of Chemistry of the University of Milan. Mass spectra were recorded on a Varian VG9090 Spectrometer.

2.1. Synthesis of (C₆F₅)₃SiOH (1). A stream of wet nitrogen, obtained by flowing the gas in a Drechsel's bottle filled with water, was bubbled in a two-necked flask containing $(C_6F_5)_3SiCl$ (262 mg, 0.464 mmol) dissolved in freshly distilled dichloromethane (20 mL). The reaction was continued until the gas flowing out from the reaction flask was no longer acid (*ca.* 45 min. as monitored by litmus test). The dichloromethane solution was evaporated, affording spectroscopically pure $(C_6F_5)_3SiOH$ as a white solid (221 mg, 0.404 mmol, yield 87%). NMR data $(CDCl_3, 298 K, 9.4 T)$. ^1H NMR: δ 3.56 (s, OH) (Fig. S1); ^{13}C NMR: δ 149.1 ($^1J_{C-F} = 244.0$ Hz, *ortho*), 144.1 ($J_{C-F} = 260.0$ Hz, $^2J_{CF} = 13.1$ Hz and $^3J_{CF} = 6.1$ Hz, *para*), 137.5 ($^1J_{C-F} = 256.0$ Hz, *meta*), 105.1 (t, $^2J_{C-F} = 27.6$ Hz, *ipso*) (Fig. S2); ^{19}F NMR: δ -128.1 (d, $J = 18.5$ Hz, *ortho*), -145.8 (t, $J = 19.9$ Hz, *para*), -159.1 (m, *meta*) (Fig. S3); ^{29}Si NMR: δ -30.98 (Fig. S4). MS-EI: *m/z* 546 $[M]^+$. Anal. Calcd. for $C_{18}HF_{15}OSi$: C, 39.58; H, 0.18. Found: C, 39.76; H, 0.24. Crystals suitable for X-ray diffraction were obtained from an *n*-pentane solution at 253 K.

2.2. Synthesis of (C₆F₅)₃SiOD (2). The reaction was carried out as above described, using a nitrogen flow wet with D_2O, in a two-necked flask containing $(C_6F_5)_3SiCl$ (203 mg, 0.360 mmol) dissolved in freshly distilled dichloromethane (12 mL). After completion of the reaction (*ca.* 45 min, as shown by the litmus test) the solution was evaporated, affording a white solid (158 mg, 0.289 mmol, yield 80%) characterized by ^2H and ^{19}F NMR spectroscopy (Fig. S5 and Fig S6). NMR data (9.4 T, 298 K): ^2H NMR (CH_2Cl_2): δ 3.67 (s, OD); ^{19}F NMR (CD_2Cl_2): δ -128.4 (d, $J = 18.6$ Hz, *ortho*), -147.0 (t, $J = 19.7$ Hz, *para*), -160.2 (m, *meta*).

Traces of **1**, due to the presence of adventitious water in the reaction system, were also detected, as indicated by a broad resonance at 3.82 ppm in the ^1H NMR spectrum (Fig. S7).

2.3. Reaction of 1 with Water. In a two necked flask, **1** (60 mg, 0.110 mmol) was dissolved under nitrogen in freshly distilled CH_2Cl_2 (5 mL), added with water (5 mL) and stirred one day at room

temperature. The organic phase was then separated, dried under vacuum and checked by ^{19}F NMR spectroscopy in $CDCl_3$ revealing the presence of the starting silanol (accounting for *ca.* 60% of the total fluorinated species) together with mainly two other fluorinated species (Fig. S8). This mixture was again dissolved in CH_2Cl_2 (5 mL) and stirred with water (5 mL) at room temperature for 5 days to achieve the total conversion of $(C_6F_5)_3SiOH$. The reaction crude showed the presence of several fluorinated species among which we could only identify traces of HC_6F_5 (Fig. S8). An insoluble white residue was present as well probably due to the formation of cross-linked siloxane $R_nSi(OH)_m$ moieties. NMR data ($CDCl_3$, 298 K, 9.4 T). ^{19}F NMR after 1 day: δ -128.0 (d, $J = 20.4$ Hz), -128.1 ($(C_6F_5)_3SiOH$, d, $J = 18.4$ Hz, *ortho*), -129.1 (d, $J = 19.7$ Hz), -145.0 (t, $J = 20.2$ Hz), -145.8 ($(C_6F_5)_3SiOH$, t, $J = 19.7$ Hz, *para*), -146.1 (t, $J = 20.2$ Hz), -159.1 (m). ^{19}F NMR after 5 days: δ -129.0 (m, br), -138.6 (C_6F_5H, dd, $J_1 = 21.7$ Hz, $J_2 = 8.5$ Hz, *ortho*), -145.6 (m, br), -153.6 (C_6F_5H , t, $J = 20.1$ Hz, *para*), -159.6 (m, br), -162.0 (C_6F_5H , m, *meta*).

2.4. Reaction of 1 with Butyllithium and Re(CO)₅O₃SCF₃. In a two necked flask, **1** (130 mg, 0.238 mmol) was dried 3 h at 80°C under vacuum, then dissolved at room temperature under nitrogen in freshly distilled diethyl ether (7 mL) and added with one equivalent of *n*-BuLi (0.15 mL, 0.24 mmol, 1.6 M in *n*-hexane). The reaction mixture was stirred for 30 min and then evaporated under vacuum to afford a white powder that was subsequently dissolved in freshly distilled tetrahydrofuran (10 mL) and added with the stoichiometric amount of $[Re(CO)_5O_3SCF_3]$ (113 mg, 0.238 mmol). The reaction was monitored by infrared spectroscopy, which showed the slow disappearance of the carbonyl bands of $[Re(CO)_5O_3SCF_3]$ (2164(vw), 2053(vs) and 1999(m) cm^{-1}) with the formation of a new species with bands centred at 2146(vw), 2032(vs) and 2002(m) cm^{-1}. The reaction was complete in about 6 days, when the infrared stretching bands of the reagent

could no longer be detected in the reaction mixture. After evaporation of the solvent the crude was dissolved in pentane and crystallized at -20 °C. Mass spectrometry and X-ray diffraction analysis confirmed the formation of the $[Re(CO)_5(C_6F_5)]$ complex [15,16], with no traces of the expected $[Re(CO)_5OSi(C_6F_5)_3]$ derivative. Spectroscopic data for $[Re(CO)_5(C_6F_5)]$: ν_{CO} (THF) = 2146(w), 2032(vs) and 2002 (m) cm^{-1}; ν_{CO} in pentane = 2146(w), 2038(vs) and 2004 (m) cm^{-1}. ^{19}F NMR (THF-d$_8$, 298 K, 7.05 T) δ -102.5 (m, *ortho*), -161.4 (t, *J* = 19.4 Hz, *para*), -164.6 (m, *meta*) (Fig. S9) MS-EI: *m/z* 494 [M]$^+$.

2.5. Reaction of 1 with [Re(CO)$_3$(PPh$_3$)$_2$CH$_3$]. In a Schlenk flask **1** (41 mg, 0.076 mmol) and $[Re(CO)_3(PPh_3)_2CH_3]$ (41 mg, 0.051 mmol) were dissolved in freshly distilled toluene at 110°C under nitrogen atmosphere and heated up to 50 h. The reaction was monitored by infrared spectroscopy, showing no changes in the carbonyl region were only the bands of $[Re(CO)_3(PPh_3)_2CH_3]$ (2030(vw), 1947(w), 1924(vs) and 1886(m) cm^{-1}) were detected. A ^{19}F NMR of the final reaction mixture revealed the presence of HC$_6$F$_5$ as the only fluorine-containing species (Fig. S10).

2.6. Reaction of 1 with Butyllithium. In a two-necked flask **1** (29 mg, 0.053 mmol) was dried 3 h at 80°C under vacuum, then dissolved at room temperature under nitrogen atmosphere in freshly distilled diethyl ether (5 mL) and added at room temperature with an equimolar amount of *n*-BuLi (0.033mL, 0.053 mmol, 1.6 M in *n*-hexane). The resulting clear solution was stirred for 15 min and then evaporated to dryness. NMR spectroscopy in CD$_3$CN of the reaction crude showed that all **1** was consumed to give a mixture containing HC$_6$F$_5$ and DC$_6$F$_5$ as major products together with minor amounts of unidentified species. NMR data (CD$_3$CN, 298 K, 9.4 T) ^{19}F NMR: δ -128.8 (s,

br), -140.8 (HC_6F_5, m, *ortho*), -141.0 (DC_6F_5, dd, $J_1 = 8.3$ Hz, $J_2 = 21.0$ Hz, *ortho*), -156.3 (HC_6F_5, t, $J = 19.2$ Hz, *para*), -156.4 (DC_6F_5, t, $J = 19.1$ Hz, *para*), -164.2 (m, br), -164.3 (HC_6F_5 and DC_6F_5, m, *meta*) (Fig. S11).

2.7. Reaction of 1 with NEt₃ and with 1,8-Bis(dimethylamino)naphthalene (DMAN or proton sponge).

The reactions have been performed directly into NMR tubes and monitored by NMR spectroscopy. In a typical reaction **1** (31 mg, 0.057 mmol) was dissolved in CD_2Cl_2 and cooled to 195 K. After addition of the base, the NMR spectra were collected, usually at temperatures in the 221-236 K range. The ^{19}F NMR spectra revealed that upon addition of 1 equivalent of base (either NEt₃ or proton sponge) all silanol **1** was reacted, giving HC_6F_5 (accounting for ca. 40% of the total fluorinated species in solution) together with a mixture of unidentified species (see Fig. S12 and S13). Some precipitate was also present in the tubes. Similar results were obtained when adding a catalytic amount of DMAN (0.1 eq.). In this latter case, besides the resonances of HC_6F_5, ^1H NMR showed the signals related to protonated proton sponge DMANH⁺ in a 1:6 ratio with respect to the free base DMAN (Fig. S14).

NMR data (CD_2Cl_2):

(**a**) sample treated with 1 equivalent of NEt₃ (227 K, 9.4 T): ^1H NMR: δ 7.03 (m, HC_6F_5), 2.45 (q, J = 6.1 Hz, N(CH_2CH_3)₃), 0.96 (t, J = 6.1 Hz, N(CH₂CH_3)₃). ^{19}F NMR: δ main signals -129.2 (m), -138.9 (C_6F_5H , m, *ortho*), -145.7 (m), -154.1 (t, $J = 20.7$ Hz, *para*, HC_6F_5), -159.7 (m), -162.3 (HC_6F_5, m, *meta*);

(**b**) sample treated with 1 equivalent of proton sponge (221 K, 11.7 T): ^1H NMR DMAN: δ 7.33 (m, 4H), 6.94 (d, 2H, J=7.2 Hz), 2.78 (s, 12H); HC_6F_5: 7.02 (m, 1H). ^{19}F NMR main signals:

δ -129.2 (m), -138.8 (dd, J_1 = 22.8 Hz, J_2 = 8.4 Hz, *ortho* HC_6F_5), -145.6 (m), -154.0 (t, J = 21.0 Hz, *para* HC_6F_5), -159.7 (m), -162.2 (m, *meta*, HC_6F_5);

(**c**) 0.1 equivalent of proton sponge (236 K, 9.4 T): ^{1}H NMR: δ 19.33 (s, 1H, NH^+), 8.00 (d, 2H, J=8.2 Hz, $DMANH^+$), 7.82 (d, 2H, J=7.8 Hz, $DMANH^+$), 7.69 (t, 2H, J=7.8 Hz, $DMANH^+$), 7.32 (m, 4H, DMAN), 7.02 (m, 1H, HC_6F_5), 6.93 (d, 2H, J=7.1 Hz, DMAN), 3.34 (s, 12H, $DMANH^+$) 2.77 (s, 12H, DMAN) ppm. ^{19}F NMR: δ -129.2 (m, br), -138.9 (m, *ortho*, HC_6F_5), -145.7 (m, br), -154.2 (t, J = 20.6 Hz, *para*, HC_6F_5), -159.8 (m), -162.3 (m, *meta*, HC_6F_5).

2.8. Reactivity of 2 with 0.1 equivalent of 1,8-Bis(dimethylamino)naphthalene (DMAN or proton sponge).

Addition at 237 K of 0.1 equivalent of proton sponge to a sample of **2** dissolved in CD_2Cl_2 caused immediately its complete decomposition into a mixture of unidentified compounds (probably oligomeric species) with several resonances, one of which is prevalent, in the typical region for pentafluorophenyl silicon compounds [12,17] (Fig. 5 and S15), together with both DC_6F_5 and HC_6F_5 (in a 7:3 ratio and accounting for ca. 45% of total fluorinated species in solution. Moreover, ^{1}H NMR showed the presence, besides the signals for HC_6F_5, of proton sponge and protonated proton sponge $DMANH^+$ (in approximately a 1:17 ratio with respect to the free base DMAN).

^{1}H NMR (CD_2Cl_2, 273 K. 9.4 T): HC_6F_5 = δ 7.02 (m, 1H). Proton sponge = δ 7.32 (m, 4H), 6.93 (d, 2H, J=7.1 Hz), 2.77 (s, 12H). Protonated proton sponge = δ 8.03 (d, 2H, J=8.1 Hz), 7.82 (m, br, 2H), 7.72 (m, br, 2H), 3.29 (s, 12H). ^{19}F NMR (CD_2Cl_2, 236 K): δ -129.2 (m, br), -138.9 (m, *ortho*, HC_6F_5), -139.2 (dd, J_1 = 8.2 Hz, J_2 = 22.1 Hz, *ortho*, DC_6F_5), -145.7 (m, br), -154.2 (t, J = 20.6 Hz, *para*, HC_6F_5), -154.3 (C_6F_5D , t, J = 20.6 Hz, *para*), -159.8 (m, br), -162.4 (m, *meta*, HC_6F_5 and DC_6F_5).

2.9. Reactivity of 1 with triflic acid (CF₃SO₃H). The reaction was carried out in an NMR tube and monitored by ^{19}F NMR spectroscopy. A sample of **1** (35 mg, 0.064 mmol) was dissolved in CD_2Cl_2 (0.75 mL) in an NMR tube and added with $CH_3C_6F_5$ (9.2 µL, 0.073 mmol) as internal standard (to ascertain if the reaction would cause any decrease of the overall amount of species in solution). After the addition of 1 equivalent of triflic acid, the ^{19}F NMR spectrum showed the partial conversion of the perfluorinated silanol into the silyl triflate product $(C_6F_5)_3SiOSO_2CF_3$ (ratio triflate:silanol = 1:3, Fig. S16). Further additions of triflic acid caused a significant increase of the amount of product (ratio triflate:silanol = 2:1 after addition of total 3 equivalents of CF_3SO_3H). ^{19}F NMR data for $(C_6F_5)_3SiOSO_2CF_3$ (CD_2Cl_2, 298 K, 9.4 T): δ -76.1 (s, CF_3), -126.2 (d, J = 16.8 Hz, *ortho*), -142.6 (t, J = 18.3 Hz, *para*), -158.6 (pseudo-t, J = 16.4 Hz, *meta*), in good agreement with literature data [18].

2.10. X-ray Structural Analysis of [(C₆F₅)₃SiOH]₂(C₅H₁₂) and [Re(CO)₅(C₆F₅)]. Diffraction data have been collected on a Bruker SMART diffractometer and empirically corrected for absorption [19]. The structures were solved by direct methods (SIR97) [20] and subsequent Fourier syntheses and eventually refined by full-matrix least-squares on $F_o{}^2$ (SHELX-97) [21] with WINGX [22] interface. Anisotropic thermal factors were assigned to all non-hydrogen atoms (but one of the two disordered clathrate pentane molecules in $[(C_6F_5)_3SiOH]_2(C_5H_{12})$), all hydrogen atoms were placed in idealized position and refined with a common isotropic thermal factor. Relevant crystal data and refinements details are reported in the Supporting Information (Table S1).

CCDC 2100804 and 2096538 contain the supplementary crystallographic data for $[(C_6F_5)_3SiOH]_2$(*n*-pentane) and $[Re(CO)_5(C_6F_5)]$, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre http://www.ccdc.cam.ac.uk/conts/retrieving.html.

3. Results and discussion

3.1. Synthesis of (C₆F₅)₃SiOH (1). Hydrolysis of chlorosilanes is one of the most common synthetic ways to obtain silanols. The reaction is usually carried out in a two-phase system, under rigorous control of the solution pH, to avoid self-condensation and polymerization [23]. Attempts to hydrolyze $(C_6F_5)_3SiCl$ [12] in biphasic systems (i.e. toluene/water, CH_2Cl_2/water or Et_2O/water), by changing several times the aqueous layer until neutral pH, as described for the synthesis of $(C_6H_5)_2Si(OH)_2$ from $(C_6H_5)_2SiCl_2$ [24] invariably failed. The use of a different procedure, the one described for the preparation of lower molecular weight silanols involving a two-phase hydrolysis in the presence of a proton acceptor such as ammonium bicarbonate [25], was not successful as well. Usually, the reaction crudes showed the formation of a white residue (likely a polysiloxane derivative) that was soluble only in HF 10%, together with a mixture of fluorinated products among which we could recognize only HC_6F_5 (identified by its characteristic ^{1}H NMR and ^{19}F NMR multiplets) [26]. The presence of pentafluorobenzene in the reaction crudes suggested that $(C_6F_5)_3SiOH$, once formed, could easily undergo stepwise replacement of its aryl substituent with the production of C_6F_5H (Equation 1), similarly to the known reactivity of monomeric perfluorophenylboranes [27,28] and borates [29] in the presence of water. The cleavage of $Si-C_6F_5$ bonds by reaction with water to give HC_6F_5 (equation 1) had also been previously observed for perfluoroarylated silicon compounds like $(C_6F_5)_4Si$ [30], $(C_6F_5)SiMe_3$ [31] and the pentafluorophenyltetrafluorosilicate $[(C_6F_5)SiF_4]^-$ anion [32].

$$(C_6F_5)_3SiOH \ + \ x\,H_2O \quad \rightarrow \quad (C_6F_5)_{3\text{-}x}Si(OH)_{1+x} \ + \ x\,HC_6F_5 \qquad\qquad (\text{Eq. 1})$$
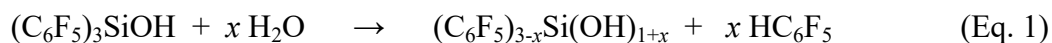
We finally succeeded in performing the controlled hydrolysis of $(C_6F_5)_3SiCl$ through the following procedure. A stream of wet nitrogen, obtained by flowing the gas in a Drechsel's bottle filled with water, was bubbled into a solution of $(C_6F_5)_3SiCl$ dissolved in freshly distilled dichloromethane. The reaction was monitored until the gas, flowing out from the reaction flask, was no longer acid. As soon as the hydrolysis was complete, the wet nitrogen stream was stopped and the dichloromethane solution was quickly evaporated to afford pure $(C_6F_5)_3SiOH$ (yield 87%). The product was characterized by ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR (see Supporting Information Figures S1-S4) and mass spectroscopies, elemental analysis and X-ray diffraction. ^{1}H NMR showed only one signal due to the hydroxyl group (δ 3.56 ppm, in CDCl$_3$), while ^{13}C and ^{19}F NMR displayed the typical features of compounds containing perfluorinated aromatic rings [12,18] (see Experimental part). ^{29}Si NMR was characterized by a resonance at -30.96 ppm that falls in the same region of the chemical shifts reported for other $(C_6F_5)_3SiOR$ derivatives [17]. The mass spectrum obtained by electron impact ionization showed the molecular peak [M]$^+$ at 546 *m/z*, with the expected isotopic distribution.

3.2. X-ray Structure of $(C_6F_5)_3SiOH$ (1). Elongated colourless crystals of a solvate derivative of stoichiometry $[(C_6F_5)_3SiOH]_2$(pentane) have been obtained from *n*-pentane solutions at 253 K. The isolated crystals were very unstable upon mother liquor removal, and their solid-state structure was elucidated by X-ray diffraction analysis at 100 K, showing the presence of two independent silanol molecules, which are illustrated in Figure 1. Selected bond distances, angles, and torsional angles defining the geometry around the silicon atoms are reported in Table 1. Crystal data and details of the structure refinement are reported in the Supporting Information (Table S1).
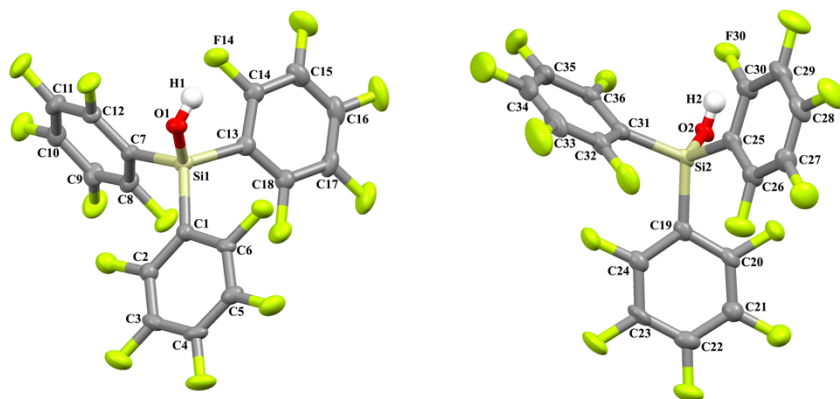
11

Figure 1. Views of the two independent silanol molecules in [(C₆F₅)₃SiOH]₂(*n*-pentane), showing a partial atom-labelling scheme. Thermal ellipsoids are drawn at 50% probability level.

The major structural feature in the solid state is the presence of rather short intermolecular O–H···O hydrogen bonds (as judged from the O···O distances, see Table 2), organised in a folded $R_4^4(8)$ ring synthon of D_{2d} symmetry (a flattened tetrahedron), affording a cyclic tetramer of approximate S_4 symmetry, lying about a two-fold crystallographic axis, as illustrated in Figure 2.
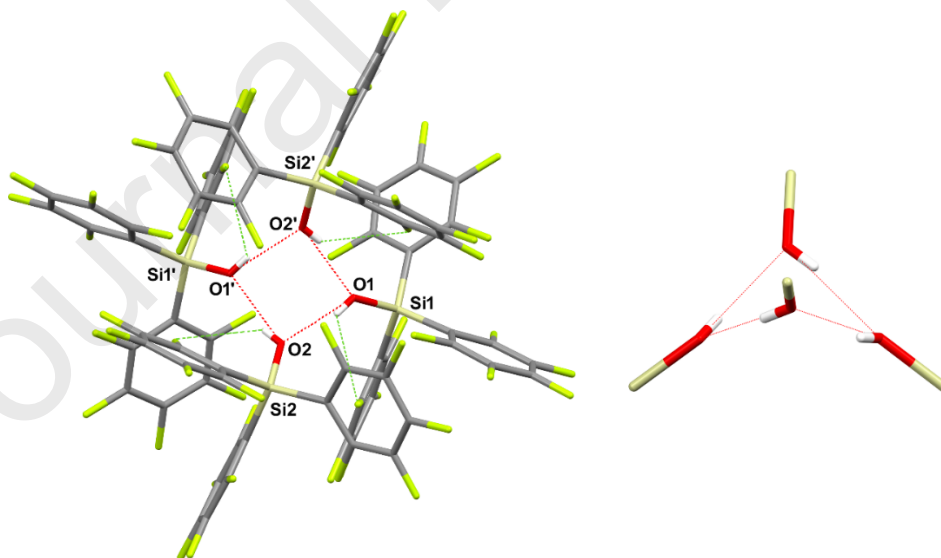

Figure 2. A view of the cyclic [(C₆F₅)₃SiOH] tetramer of idealised S_4 symmetry (left). A lateral view of the folded $R_4^4(8)$ ring synthon of idealised D_{2d} symmetry (right). Symmetry code ('): [-x, y, -z + 1/2].

A search in the Cambridge Structural Database (CSD version 5.42) for the analogous hydrogenated molecule $(C_6H_5)_3SiOH$ resulted in a series of structures comprising the solvent free species [33,34] and different adducts including those with dioxane [35], dimethyl sulfoxide, ethanol, 12-crown-4 [36], and triphenylphoshine oxide [37]. A comparison of all these structures evidenced that the main differences concern the supramolecular solid state packing that is strongly influenced by the hydrogen bond patterns. Within the single silanol molecule a difference is observed in the Si–O distance which is shorter in the present structure [1.621(3) and 1.618(3) Å] with respect to the values found for the free $(C_6H_5)_3SiOH$ molecule [range 1.640-1.647 Å at low temperature] and for its adducts [range 1.620-1.639 Å]. The shortening of the Si–O distance is probably due to the electron-withdrawing effect of the perfluorophenyl groups that enhances the π-back donation from the oxygen to the silicon atom; a similar feature has been observed for $(C_6F_5)_3SiOMe$ [38] with respect to $(C_6H_5)_3SiOMe$ [38] [Si–O distances 1.597 Å at 120K and 1.632 Å at RT, respectively]. Moreover, short intramolecular contacts are found between one of the two *ortho* fluorine atoms of a perfluorophenyl ring and the acidic hydrogen atom of the hydroxyl group (see Fig. 2 and Table 2).

Supramolecular analysis of the selected crystal structures containing the silanol $(C_6H_5)_3SiOH$ shows that only the free molecule shows cyclic tetramers resembling those found in the present structure. Different oligomers are recognized in all the adducts due to the involvement of the co-crystallized molecules in the hydrogen bonding patterns. Dioxane, DMSO, 12-crown-4, and triphenylphoshine oxide molecules, acting as hydrogen bond acceptors, bind respectively four, two, two, and one molecules of silanol. Differently, ethanol, being a hydrogen bond donor/acceptor, gives rise to cyclic oligomers formed by one ethanol and four silanol molecules through the $R_3^5(10)$ ring synthon.

Hence, cyclic tetramers are preferred when the silanol molecules are the only species able to act as donors and acceptors of hydrogen bonds, as in the present structure and in that of $(C_6H_5)_3SiOH$. In the fluorinated species, however, a less compact packing is observed, due to the presence of disordered *n*-pentane molecules, one of which is disordered along a 2-fold symmetry axis in the direction of the crystallographic **b** axis and the second lying on an inversion centre (see Fig. 3). The free space, evaluated after removing the pentane molecules, accounts for *ca*. 21 % of the total cell volume.

A more detailed inspection of the structure reveals also the presence of F···F and C–F···π_F intermolecular interactions which contribute to the molecular packing. In particular, two C–F···π_F interactions are recognized within the tetramer [F12···$Cg_{(C19-C24)}$ 3.101(3) Å, C–F···Cg 123.9(2)° and F36···$Cg_{(C1-C6)}$ 3.254(3) Å, C–F···Cg 111.4(2)°; Cg indicate the barycentre of the relative aromatic ring], while inter-tetramers interactions produces supramolecular undulated chains along the crystallographic **c** axis [F8···$Cg_{(C1-C6)}$ 3.281(3) Å, C–F···Cg 135.4(2)°] which are further connected to give a 3D supramolecular network [F10···$Cg_{(C31-C36)}$ 3.140(3) Å, C–F···Cg 145.6(2)°]. Simplifying the tetramers to their barycentres and taking into account the C–F...πF interactions it results that the 3D supramolecular network show the topology observed in moganite (**mog**) [39]. It is interesting to note that in the structure of $(C_6H_5)_3SiOH$ neither C–H···π nor aromatic π···π interactions were detected.
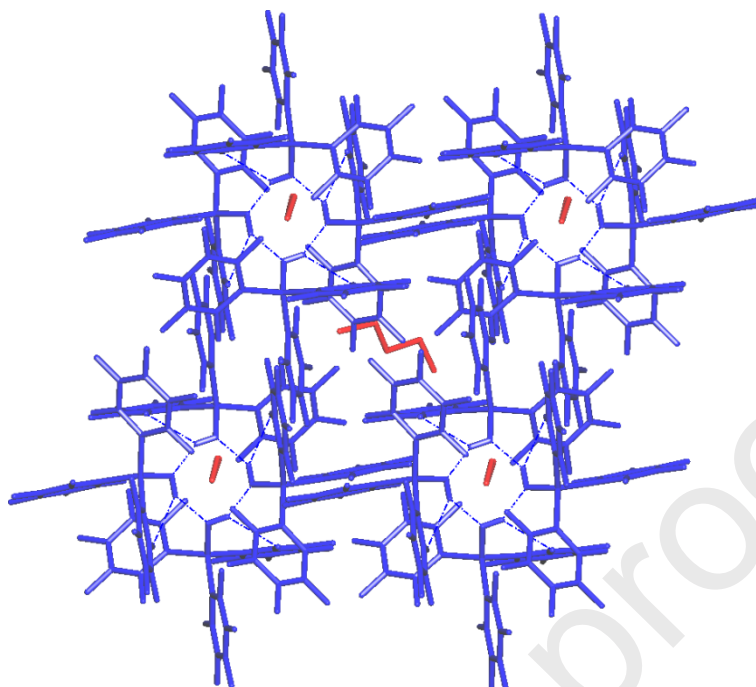
Figure 3. A view down the crystallographic **b** axis showing the packing in $[(C_6F_5)_3SiOH]_2(n\text{-}$ pentane). For the sake of clarity, only one model for both disordered pentane molecules is shown in red.

Table 1. Selected bond lengths (Å) and angles (°) for $[(C_6F_5)_3SiOH]_2(n\text{-pentane})$.

Si1–O1	1.6 21(3)
Si1–C1	1.8 69(4)
Si1–C7	1.874(4)
Si1–C13	1.869(4)
O1–Si1–C1	105.3(2)
O1–Si1–C7	112.0(2)
O1–Si1–C13	110.0 (2)
C1–Si1–C7	112.6(2)
C1–Si1–C13	104.7(2)
C7–Si1–C13	104.8(2)
Si1–C1–C2	127.0(3)
Si1–C1–C6	117.7(3)

O1–Si1–C1–C2	115.8(3)
O1–Si1–C7–C8	-179.3(3)
O1–Si1–C13–C14	-51.6(3)
Si2–O2	1.61 8(3)
Si2–C19	1.867(4)
Si2–C25	1.870(4)
Si2–C31	1.864(4)
O2–Si2–C19	106.6(2)
O2–Si2–C25	110.6(2)
O2–Si2–C31	111.7(2)
C19–Si2–C25	110.7(2)
C19–Si2–C31	112.0(2)
C25–Si2–C31	105.4(2)
Si2–C19–C20	119.1(3)
Si2–C19–C24	126.0(3)
O2–Si2–C19–C20	68.2(3)
O2–Si2–C25–C26	-133.3(3)
O2–Si2–C31–C32	-171.9(3)

Table 2. Hydrogen-bonding geometry (Å, °) for $[(C_6F_5)_3SiOH]_2(n\text{-pentane})$. The D-H bond distance was taken as 0.82 Å.

| D–H⋯A	H⋯A	D⋯A	D–H⋯A
O2–H2⋯O1$^{(')}$	2.03	2.716(4)	141
O1–H1⋯O2	2.03	2.686(3)	137
O1–H1⋯F14	2.41	2.988(3)	129
O2–H2⋯F30	2.37	2.985(3)	132

$^{(')}$1-x,y,1/2-z

3.3. Reactivity of 1 with water. The difficulties met during the hydrolysis of $(C_6F_5)_3SiCl$ to its corresponding silanol in biphasic water/solvent systems suggested that **1** might be very reactive toward water, with cleavage of the $Si\text{-}C_6F_5$ bond and formation of HC_6F_5 (Equation 1), in agreement with the previously mentioned literature data [30–32]. To test this hypothesis an equal volume of water was added to a CH_2Cl_2 solution of $(C_6F_5)_3SiOH$ and the mixture was stirred

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overnight at room temperature. After evaporation to dryness of the organic phase, a ^{19}F NMR spectrum in CDCl$_3$ of the residue revealed that the starting silanol was still present (accounting for ca. 60% of the total fluorinated species), together with two other main unidentified fluorinated species (see Supporting Information Figure S8). This mixture was again dissolved in CH$_2$Cl$_2$ and treated with a large excess of water: after 5 days all (C$_6$F$_5$)$_3$SiOH was converted into several fluorinated species, among which we could identify some HC$_6$F$_5$ (see Supporting Information Figure S8). An insoluble white residue was present as well. The quite long time required for decomposition with water, compared with the much faster decomposition of (C$_6$F$_5$)$_3$SiCl in the presence of excess water, indicates that the hydrochloric acid produced by hydrolysis of (C$_6$F$_5$)$_3$SiCl accelerates the condensation process. Actually, it is well known that the condensation processes of silanols are acid or base-catalyzed [23].

3.4. Reactivity of 1 with Butyllithium and Re(CO)$_5$O$_3$SCF$_3$. By using the methodology successfully employed for the synthesis of the [Re(CO)$_5$OR] complex containing the silsesquioxane derivative (*c*-C$_6$H$_{11}$)$_7$Si$_8$O$_{12}$O$^-$ [9], we reacted (C$_6$F$_5$)$_3$SiOH with butyllithium and then with [Re(CO)$_5$O$_3$SCF$_3$] in tetrahydrofuran solution at room temperature under nitrogen. The reaction was monitored by infrared spectroscopy and showed the slow disappearance of the carbonyl bands of [Re(CO)$_5$(O$_3$SCF$_3$)] (at 2164(vw), 2053(vs) and 1999(m) cm^{-1}) with the formation of a new species, whose ν(CO) bands maintain the typical pattern of rhenium pentacarbonyl complexes [40]: 2146(vw), 2038(vs) and 2004(m) cm^{-1}. The reaction was very slow and went to completion in about 5-7 days, when the infrared stretching bands of the reagent could no longer be detected in the reaction mixture. After evaporation of the solvent, the crude was dissolved in pentane and crystallized at 253 K, affording stable colourless prismatic crystals. Their

X-ray diffraction analysis, carried out at room temperature, surprisingly revealed that the isolated species was not the expected $[Re(CO)_5OSi(C_6F_5)_3]$ complex, but rather the known pentafluorophenyl derivative $[Re(CO)_5(C_6F_5)]$ [16,41]. To our knowledge, the X-ray structure of this compound has never been reported in the literature, so it will be briefly discussed here. It is possible that, treatment with BuLi, produced a small fraction of silanolate anion $(C_6F_5)_3SiO^-$, initiating a polymerization process. The process resulted in the elimination of the $C_6F_5^-$ moiety, as depicted in Scheme 1, which further reacted with the rhenium pentacarbonyl triflate to give $Re(CO)_5(C_6F_5)$."
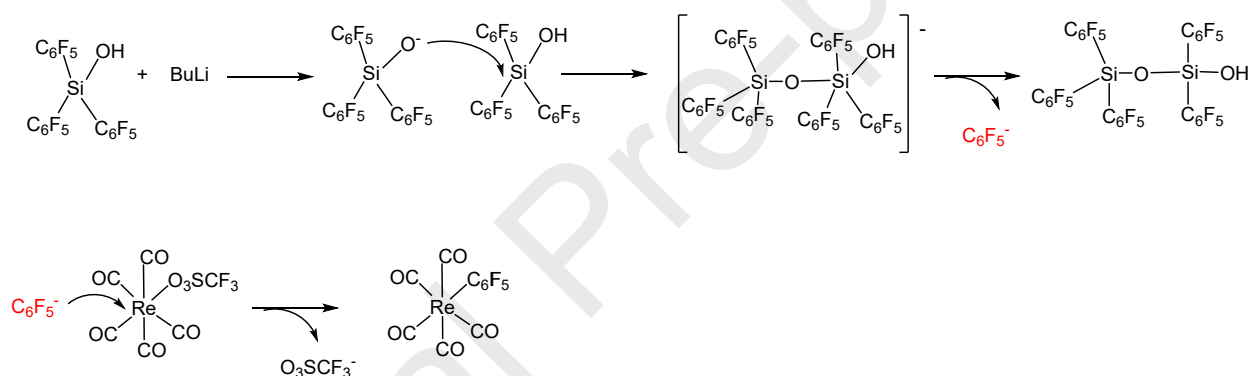
Scheme 1. Top: Oligomerization process of $(C_6F_5)_3SiOH$ promoted by BuLi. Bottom: Formation of the $Re(CO)_5(C_6F_5)$ complex.

3.4.1 X-ray Structure of [Re(CO)$_5$(C$_6$F$_5$)]. The asymmetric unit contains three independent (half) molecules lying on the mirror planes of the $P2_1/m$ space group as shown in Fig. 4. The stereochemistry of the octahedral $[Re(CO)_5(C_6F_5)]$ molecule, of idealized C_{2v} symmetry, shows, as expected, the perfluorinated phenyl ring staggered with respect to the four equatorial carbonyls. The average Re-C$_{PF}$, Re-C(O)$_{eq}$ and Re-C(O)$_{ax}$ bond lengths are 2.218, 2.008 and 1.958 Å,

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respectively. The equatorial carbonyls are slightly bent away from the axial ones: average C_{ax}-Re-C_{eq} 90.96°. Selected bond distances and angles are listed in Table 3. Crystal data and details of the structure refinement are reported in the Supporting Information (Table S1).
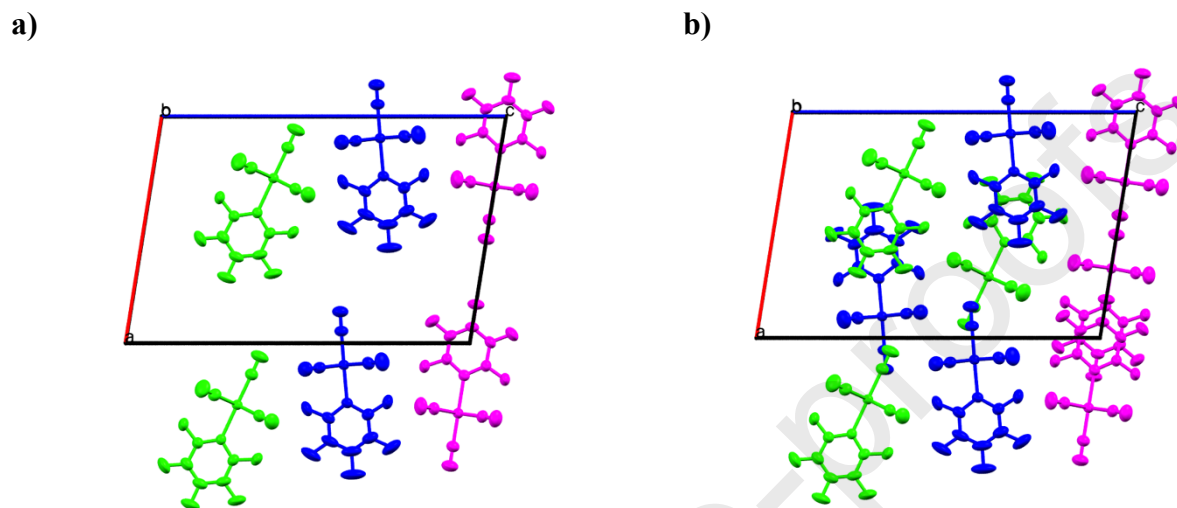
a)   **b)**

Figure 4. a) View (down **b**) of the in plane (y=0.25) organisation of the three crystallographically independent $[Re(CO)_5(C_6F_5)]$ (half) molecules (1-3, green, blue and magenta, respectively). b) Adjacent planes are related by a $P2_1$ screw axis (.5, y, .5) thus green and blue aromatic rings are hetero-stacked while the magenta ones are self-stacked, the stacking separation being of 3.705 Å (b/2). Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected bond lenghts (Å) and angles (°) for $[Re(CO)_5(C_6F_5)]$.

Molecule	n=1	n=2	n=3
Re(n)-C(n1)	1.956(6)	1.967(5)	1.951(6)
Re(n)-C(n2)	2.009(4)	2.013(4)	2.011(4)
Re(n)-C(n3)	2.007(4)	1.999(4)	2.009(4)
Re(n)-C(n11)	2.219(5)	2.212(5)	2.222(5)
C(n1)-O(n1)	1.137(7)	1.132(6)	1.148(7)
C(n2)-O(n2)	1.113(5)	1.119(5)	1.126(5)
C(n3)-O(n3)	1.128(4)	1.126(4)	1.121(5)
C(n11)-C(n12)	1.370(7)	1.380(7)	1.388(7)
C(n11)-C(n16)	1.392(7)	1.397(7)	1.386(7)
C(n12)-C(n13)	1.374(8)	1.360(8)	1.374(7)
C(n13)-C(n14)	1.372(9)	1.337(11	1.365(8)
C(n14)-C(n15)	1.368(9)	1.385(11	1.371(8)
C(n15)-C(n16)	1.368(8)	1.361(8)	1.391(7)

C(n12)-F(n2)	1.363(6)	1.354(7)	1.349(6)
C(n13)-F(n3)	1.334(7)	1.357(8)	1.340(6)
C(n14)-F(n4)	1.332(6)	1.349(7)	1.336(6)
C(n15)-F(n5)	1.354(6)	1.346(8)	1.343(6)
C(n16)-F(n6)	1.364(6)	1.365(7)	1.352(6)
C(n1)-Re(n)-C(n2)	90.8(2)	90.3(2)	91.4(2)
C(n1)-Re(n)-C(n3)	90.9(2)	91.6(2)	90.8(2)

3.5. Reaction of 1 with [Re(CO)$_3$(PPh$_3$)$_2$CH$_3$]

The impossibility of obtaining [Re(CO)$_5$OSi(C$_6$F$_5$)$_3$] through the above methodology prompted us to pursue a different approach. It has been reported that the stable aryloxide derivative [Re(CO)$_3$(PPh$_3$)$_2$(OC$_6$H$_4$CH$_3$)] can be prepared by treatment of the methyl complex [Re(CO)$_3$(PPh$_3$)$_2$CH$_3$] with *p*-cresol CH$_3$C$_6$H$_4$OH [42]. The reaction is based on the acidity of the protonated form of the entering OR ligand. Tris(pentafluorophenyl)silanol (**1**) is expected to be quite acidic, although no direct pK$_a$ determination could be carried out by conventional acid-base titration methods [43], due to its complete decomposition when contacted with bases (vide infra). However, a qualitative estimate of the relative acidity of **1** compared to *p*-cresol and (C$_6$H$_5$)$_3$SiOH was obtained by measuring the Δν change in the O-H stretching frequency between the free OH group and the one involved in hydrogen bonding with a suitable base, such as diethylether [44,45]. For **1** a Δν = 522 cm^{-1} was measured (in CCl$_4$), which was almost twice as large as the one observed for *p*-CH$_3$C$_6$H$_4$OH and (C$_6$H$_5$)$_3$SiOH (Δν = 267 cm^{-1} and 314 cm^{-1} respectively, see Supporting Information, Figures S17-S19 and Scheme S1). Therefore, **1** can be considered a stronger acid than (C$_6$H$_5$)$_3$SiOH and *p*-cresol, at least from the point of view of the hydrogen-bond acidity, with an estimated pK$_a$ lower than that of (C$_6$H$_5$)$_3$SiOH (equal to 16.57) [46].

Accordingly, we investigated the reactivity of [Re(CO)$_3$(PPh$_3$)$_2$CH$_3$] with **1**, but the reaction (toluene, 110 °C, up to 50 h) did not give the wished results. Indeed, pentafluorobenzene was the only fluorine-containing species detectable by ^{19}F NMR in the final reaction mixture (see

Supporting Information, Figure S10, in which some white gummy precipitate was also present. Similar results were obtained in the reaction of **1** with-[Re(CO)$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)CH$_3$]. These results suggest that protonation of the methyl group did occur, but the resulting silanolate anion underwent dearylation and/or condensation to insoluble oligomers, in line with the behaviour of **1** in the presence of bases, described in the following paragraph.

3.6. Reaction of 1 with bases: butyllithium, NEt$_3$ and proton sponge (1,8-Bis(dimethylamino)naphthalene, DMAN). The above-described results, and in particular, the failure in the reaction between [Re(CO)$_5$O$_3$SCF$_3$] and BuLi/**1** stimulated us to investigate the reactivity of the perfluorinated **1** with butyllithium to check if the formation of the corresponding silanolate does occur. A sample of **1**, dissolved in Et$_2$O, was added at room temperature with an equimolar amount of BuLi (1.6 M in hexanes). The solution remained clear, contrarily to what observed in the similar reaction of the non-fluorinated analogue (C$_6$H$_5$)$_3$SiOH, which gave the instantaneous formation of a white precipitate of (C$_6$H$_5$)$_3$SiOLi [47,48]. Evaporation of the solvent after 15 min afforded a white residue, whose ^{19}F NMR spectrum in CD$_3$CN showed that all (C$_6$F$_5$)$_3$SiOH was consumed to give a mixture containing HC$_6$F$_5$ and DC$_6$F$_5$ as major products together with minor amounts of unidentified species (Fig. S11). This behaviour further supports the mechanism proposed in Scheme 1, suggesting that the silanolate anion (C$_6$F$_5$)$_3$SiO$^-$, if formed, is not stable in the reaction conditions and it readily loses one or more pentafluorophenyl ligands and self-condenses to give a mixture of oligomers responsible for the broad peaks in the ^{19}F aromatic region of the spectrum. The presence of HC$_6$F$_5$ and DC$_6$F$_5$ is explainable by reactivity of the C$_6$F$_5$$^-$ moiety with adventitious water and some deuterated water (or HDO) present in the CD$_3$CN solvent used to acquire the NMR spectrum at room temperature.

To establish if the instability was peculiar of the reaction with BuLi, the much less basic NEt_3 ($pK_b = 3.25$) was used and the reaction progress was monitored by carrying out the reaction directly into an NMR tube. Addition at 227 K of 1 equivalent of this base to a sample of **1**, dissolved in CD_2Cl_2, immediately caused its total decomposition, as revealed by ^{19}F NMR spectroscopy, which showed the signals of HC_6F_5 (accounting for ca. 40% of the total fluorinated species in solution) together with other resonances of minor intensity falling in the typical region for perfluorinated silicon compounds [12,17] (-129.2, -145.6, -159.7 ppm, see Fig. S12). These latter signals, at quite similar chemical shifts, are probably due to the formation of some oligomeric chains of variable lengths. An insoluble residue, which precipitated in the NMR tube, was present as well, possibly attributable to the longer oligomers. In this case, as well as in the following investigation on the reactivity of **1** with DMAN (*vide infra*), the formation of DC_6F_5 was not observed in the reaction mixture, probably due to the low temperature and to the use of a less hygroscopic solvent like CD_2Cl_2.

Analogous behaviour was observed by using the base DMAN, which is a stronger base ($pK_b = 1.90$) than NEt_3, but contrary to both butyllithium and NEt_3, it is non-nucleophilic. Interestingly, when one equivalent of DMAN was used, ^{1}H NMR revealed that the proton sponge was mainly in its non-protonated form (Fig. S13), suggesting that the formation of a small fraction of silanolate is enough to start an oligomerization process similar to the one depicted in Scheme 1.

This was confirmed by performing the reaction, under the same conditions (CD_2Cl_2 at 236 K) in the presence of a catalytic amount (0.1 equivalents) of proton sponge. The ^{19}F spectrum of the reaction mixture (Fig. S14) was very similar to the one observed using 1 equivalent of proton sponge, but also in this case, the ^{1}H NMR spectrum showed that only a small amount of proton sponge was protonated (*ca.* 15%, corresponding to 0.015 equivalents with respect to the silanol),

the remaining being still present as free base (Fig. S14). The latter observation proved that the oligomerization process can be initiated by a catalytic amount of base: as soon as one silanolate anion is formed, it quickly attacks another silanol molecule, affording a very unstable intermediate, which subsequently loses a $C_6F_5^-$ moiety and generates a novel silanolate anion with a longer chain [23]. Hence, all these experiments suggest that the formation of even a small fraction of silanolate is sufficient to start the oligomerization process.

To verify whether the H atom of pentafluorobenzene did originate from silanol or from an external proton source, the reaction with 0.1 equivalents of proton sponge was repeated using the deuterated derivative $(C_6F_5)_3SiOD$ (**2**), prepared by performing the hydrolysis of $(C_6F_5)_3SiCl$ with a flow of N_2 saturated with D_2O. The ^{19}F NMR spectrum showed that most of pentafluorobenzene was constituted by the deuterated isotopomer DC_6F_5 (DC_6F_5/HC_6F_5 ratio 7:3, Fig. 5 and Fig. S15), the presence of HC_6F_5 probably due to some unavoidable adventitious water present on the glassware, in the deuterated solvent and the reagents used.
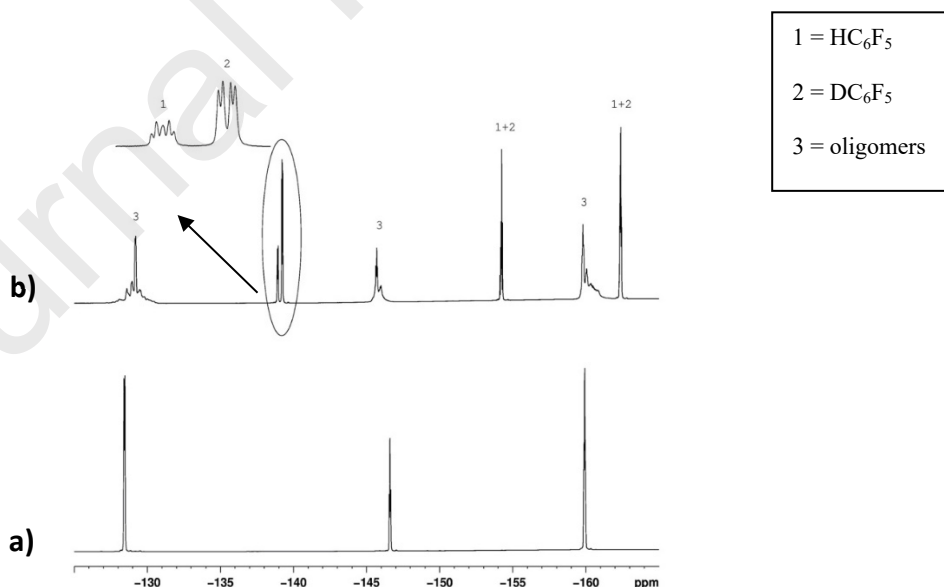

Figure 5. ^{19}F NMR (CD_2Cl_2, T = 237 K) of: a) $(C_6F_5)_3SiOD$; b) Reaction mixture right after the addition of 0.1 equivalents of proton sponge to $(C_6F_5)_3SiOD$.

3.7. Reaction of 1 with triflic acid. The complex reactivity of **1** with bases, compared to its triphenyl analogue, suggested investigating also its reactivity with strong acids. The above-described studies on the hydrolysis of $(C_6F_5)_3SiCl$ showed that aqueous HCl can easily promote the oligomerization of **1**. It was therefore of interest to investigate the behavior of **1** in the presence of a strong, poorly nucleophilic acid, such as CF_3SO_3H (triflic acid), in the absence of water. The reaction was carried out directly in an NMR tube at room temperature. Upon addition of 1 equivalent of CF_3SO_3H to a CD_2Cl_2 solution of **1**, the conversion of a fraction (*ca.* 25%) of the perfluorinated silanol into tris(pentafluorophenyl)silyl triflate $(C_6F_5)_3SiOSO_2CF_3$, identified on the bases of its ^{19}F resonances (-126.2, -142.6, -158.6 ppm) [18], was observed, according to equation 2. Further addition of triflic acid shifted the equilibrium to the right, and with a total of 3 equivalents of triflic acid, about two-thirds of **1** were converted into the silyl triflate.

$$(C_6F_5)_3SiOH + CF_3SO_3H \rightleftharpoons (C_6F_5)_3SiOSO_2CF_3 + H_2O \qquad (Eq.\ 2)$$

The fraction of **1** not converted into the silyl triflate showed a slight shift of its ^{19}F signals (-128.5, -146.9, -160.2 ppm) and the ^1H OH singlet shifted from 3.76 ppm to 5.59 ppm on addition of 1 equivalent of triflic acid, and it further shifted to 7.24 ppm when total 3 equivalents of the acid were added (Fig. S16). Moreover, in the ^1H NMR spectrum, a minor peak attributed to triflic acid appeared at lower fields (11.5 ppm). The mediated signal in the ^1H spectrum that progressively shifts at lower fields is supposedly to derive from the exchange of the OH proton with water molecules resulting from the formation of the silyl triflate (see Eq. 2). In accordance, the ^{19}F NMR spectrum showed the presence of a singlet at -76.6 ppm corresponding to triflic acid homogeneously dissolved in the organic phase together with a minor broad signal centred at -79.0 ppm, attributable to segregated droplets of triflic acid [49].

4. Conclusion

Perfluorinated silanol **1** was prepared in high yields through a new unconventional method of hydrolysis, obtained by a controlled bubbling of wet nitrogen into a CH_2Cl_2 solution of $(C_6F_5)_3SiCl$. This new procedure allowed to avoid excess water, which caused an easy cleavage of the Si-C bond with parallel formation of C_6F_5H, and, at the same time, to remove from the reaction solution the by-product HCl, preventing in this way the oligomerization/polymerization process catalyzed by HCl.

The presence of the three pentafluorophenyl substituents severely affects the reactivity of **1** with bases including water, even in a catalytic amount, which favours, by direct interaction with the Si atom, the shift of hydrogen atom from the OH group with cleavage of the Si-C bond and formation of C_6F_5H and oligomeric/polymeric siloxanes. A similar behaviour due to the presence of water and bases had been reported for other perfluoroarylated silicon compounds such as $(C_6F_5)_4Si$ [30], $(C_6F_5)_3SiMe_3$ [31] and pentafluorophenyltetrafluorosilicate $M^+[(C_6F_5)SiF_4]^-$ [32]. An analogous behaviour towards water and bases had also been observed by some of us for the bis(pentafluorophenyl)borinic acid $(C_6F_5)_2BOH$, that was reported to undergo dearylation with formation of anionic cyclic oligomers [26].

The easy cleavage of the $Si-C_6F_5$ bond even in presence of rather weak bases prevented the isolation of the $(C_6F_5)_3SiO^-$ anion, that we planned to use for the synthesis of a monomeric $[Re(CO)_5COSiR_3]$ derivative stabilized by the $(C_6F_5)_3SiO^-$ anion, expected to be very electron withdrawing and poor nucleophilic. However, when $(C_6F_5)_3SiOH$ was reacted with butyllithium and $Re(CO)_5OSO_2CF_3$, only the formation of $[Re(CO)_5C_6F_5]$ was observed. This reactivity would suggest that $(C_6F_5)_3SiOH$ may behave in basic conditions as a very successful donor of the $C_6F_5^-$ nucleophile, like $(C_6F_5)_3SiOMe$, that was recently employed in silicon Mannich reactions carried

out through a three-component coupling of aldehydes, secondary amines and silanes [50]. However, a preliminary attempt to react $(C_6F_5)_3SiOH$ with benzaldehyde and pyrrolidine, under the optimized conditions described for $(C_6F_5)_3SiOMe$, invariably gave C_6F_5H with no traces of 1-[(pentafluorophenyl)phenylmethyl]pyrrolidine. It appears that the transfer of the proton in the presence of bases is faster than the addition of the OH group. In conclusion $(C_6F_5)_3SiOH$ cannot be considered as a facile source of C_6F_5 groups, differently from its ethers like $(C_6F_5)_3SiOMe$.

The impossibility of obtaining a stable $(C_6F_5)_3SiO^-$ anion, pushed us to investigate an alternative synthetic path for the synthesis of rhenium carbonyl derivatives of the type $[Re(CO)_3(L)_2OR]$ (L = PPh_3, $Ph_2PCH_2CH_2PPh_2$) by reacting $(C_6F_5)_3SiOH$ with $Re(CO)_3(PPh_3)_2CH_3$ and $Re(CO)_3(Ph_2PCH_2CH_2PPh_2)CH_3$, since this type of reaction has been successfully carried out with p-MeC_6H_4OH [42]. However, in all cases, the expected silylated rhenium derivatives could not be isolated. This result is quite surprising since infrared spectroscopy showed that the OH group of **1** is much more acidic than that of p-$CH_3C_6H_4OH$, even though no direct pK_a determination could be carried out by conventional acid-base titration methods [43] due to its decomposition when contacted with bases.

Reactivity with a strong acid with an anion of very low nucleophilicity such as CF_3SO_3H allowed the formation of the $(C_6F_5)_3SiOSO_2CF_3$ derivative. Such relatively easy transformation provides a new route to $(C_6F_5)_3SiOSO_2CF_3$, which has been reported to be an excellent silylating reagent in organic synthesis [18].

CRediT authorship contribution statement

Tommaso Giovenzana: investigation and writing the original draft. **Elena Lucenti:** conceptualization, investigation and writing the original draft. **Lucia Carlucci:** investigation,

writing the original draft and writing (review & editing). **Giuseppe D'Alfonso:** conceptualization, validation and writing (review & editing). **Daniela Maggioni:** investigation and writing (review & editing). **Angelo Sironi:** investigation and writing the original draft. **Elena Cariati:** supervision and funding acquisition.

All the authors have contributed to the revision and finalization of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CRediT authorship contribution statement

Tommaso Giovenzana: investigation and writing the original draft. **Elena Lucenti:** conceptualization, investigation and writing the original draft. **Lucia Carlucci:** investigation, writing the original draft and writing (review & editing). **Giuseppe D'Alfonso:** conceptualization, validation and writing (review & editing). **Daniela Maggioni:** investigation and writing (review & editing). **Angelo Sironi:** investigation and writing the original draft. **Elena Cariati:** supervision and funding acquisition.

All the authors have contributed to the revision and finalization of the manuscript.
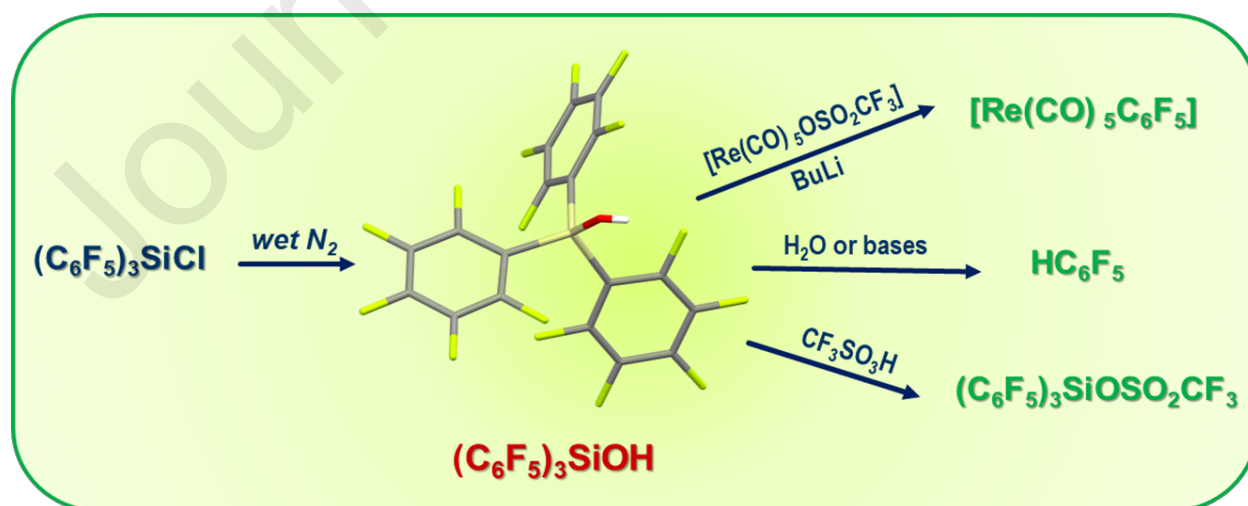
Highlights

New perfluorinated silanol $(C_6F_5)_3SiOH$ is prepared and its single crystal X-ray structure determined.

$(C_6F_5)_3SiOH$ reacts with $Re(CO)_5OSO_2CF_3$ and butyllithium to produce $[Re(CO)_5C_6F_5]$.

The $Si-C_6F_5$ bond is easily cleaved in the presence of even weak bases with formation of HC_6F_5.

Treatment of $(C_6F_5)_3SiOH$ with triflic acid gives the corresponding $(C_6F_5)_3SiOSO_2CF_3$ derivative.