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Complex Formation by Fluoroketones. I. Addition of Hexafluoroacetone to Hydrides of Group IV Elements

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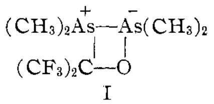
Hexafluoroacetone readily adds to trimethylsilane, trimethylgermane, and trimethyltin hydride to form 1,1,1,3,3,3-hexafluoropropoxy derivatives, and to dialkyltin dihydrides to form the bis(hexafluoropropoxy) compounds. Addition of a second mole of hexafluoroacetone to form 1:1 complexes with the propoxygermane and propoxysilane occurs at 20° in the presence of excess hexafluoroacetone. The analogous 1:1 tin complex can be isolated and is stable at 25°. Bis(1,1,1,3,3,3-hexafluoropropoxy)dimethyltin gives a stable complex containing two moles of hexafluoroacetone. The structures of the complexes and some of their reactions are discussed.

Apart from the knowledge that hexafluoroacetone forms a weak complex with trimethylarsine and a stronger one with tetramethyldiarsine, for which structure I has been suggested,[1] very little information is available about complex formation by fluoroketones. Since compounds with carbonyl groups readily from complexes with Lewis acids such as $SnBr_4$, BF_3,[2] and $(C_4H_9)_2SnCl_2$,[3] it is of interest to investigate the properties of fluoroketones as Lewis bases. Furthermore, hexafluoroacetone adds to arsenic hydrides to give arsinopropanols such as $(CH_3)_2AsC(CF_3)_2OH$, the proposed mechanism[1] involving nucleophilic attack by the arsenic lone pair on the highly electrophilic carbon atom of the carbonyl group.[4] Thus the reactions of hexafluoroacetone with group IV hydrides are of interest to see if addition occurs to give similar products. Parshall[5] has recently found that although perfluorocyclobutanone adds to phosphine to give the compound $H_2PC(OH)(CF_2)_3$ it adds to di-*n*-butylsilane in the reverse sense to give the compound $(C_4H_9)_2Si[OCH(CF_2)_3]_2$.



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Experimental

Trimethylsilane was obtained from Peninsular ChemResearch, Inc., and hexafluoroacetone from Allied Chemical Corp. Trimethylgermane was prepared from the bromide by the method of Griffiths.[6] The bromide was prepared by treating tetramethylgermane (from methylmagnesium iodide and germanium tetrachloride[7]) with bromine.[8] The alkyltin hydrides were prepared by lithium aluminum hydride reduction of the appropriate chlorides.[9] Volatile reactants and products were manipulated in a vacuum system. Reactions were carried out in sealed Pyrex tubes. Infrared spectra were recorded using a Perkin-Elmer Model 21 instrument, and n.m.r. spectra were run using Varian A-60 and H.R.-60 spectrometers. Analytical and spectroscopic data for new compounds are given in Tables I, II, and III.

(1) **Reaction of Hexafluoroacetone with Tin Hydrides.**—The reaction with trimethyltin hydride is given as a typical example. The hydride (5.0 g.) and the ketone (3.6 g.) reacted exothermally immediately on mixing. Trimethyltin hydride (1.2 g.) was recovered and the product (1,1,1,3,3,3-hexafluoropropoxy)trimethyltin (7.3 g.) condensed in a trap cooled to −46°. It distilled in a nitrogen atmosphere at 76° (58 mm.).

(2) **Reactions ot (1,1,1,3,3,3-Hexafluoropropoxy)trimethyltin.** (a) **With Hexafluoroacetone.**—Addition of excess hexafluoroacetone to the propoxytin compound was exothermic. The excess ketone was removed by pumping and the remaining 1:1 adduct, $(CH_3)_3SnOCH(CF_3)_2 \cdot (CF_3)_2CO$, melted at 23°.

(b) **With 1,1,1-Trifluoroacetone.**—There was no evidence of reaction between the propoxytin compound and trifluoroacetone. The H^1 n.m.r. spectrum showed peaks at −0.27 p.p.m. ($(CH_3)_3$-Sn–), −2.11 p.p.m. (CH_3COCF_3), and a multiplet of seven peaks (J = 6.2 c.p.s.) at −4.05 p.p.m. ($-CH(CF_3)_2$). The F^{19} n.m.r. spectrum showed a doublet due to the propoxytin compound 2.8 p.p.m. downfield from the trifluoroacetone peak.

(3) **Reaction of $(CH_3)_3SnOCH(CF_3)_2 \cdot (CF_3)_2CO$ with Trimethyltin Hydride.**—Excess complex and trimethyltin hydride were sealed in an n.m.r. tube. The H^1 spectrum taken 2 min. after mixing showed the absence of tin hydride and the presence of the propoxytin compound, $(CH_3)_3SnOCH(CF_3)_2$.

(4) **Reaction of $(CH_3)_2Sn[OCH(CF_3)_2]_2$ with the Complex $(CH_3)_2Sn[OCH(CF_3)_2]_2 \cdot 2(CF_3)_2CO$.**—The 1:2 complex of $(CH_3)_2Sn[OCH(CF_3)_2]_2$ was prepared using the procedure described in 2a above. A range of mixtures (2:1, 1:1, 1:2, 1:3) of the 1:2 complex and the bis(propoxy)tin compound when examined by H^1 n.m.r. spectroscopy always showed the presence of a third dimethyltin compound. For example, the 1:1 mixture showed peaks at −0.80, −0.92, and −1.05 p.p.m. of relative area 2:5:2, and downfield multiplets at −5.55, −5.06, and −5.11 p.p.m.

(5) **Reaction of Trimethylsilane with Hexafluoroacetone.**—The silane (2.2 g.) and excess ketone (9.0 g.) were heated at 145° (5 days). Hexafluoroacetone (3.2 g.) was recovered. The main product (5.9 g.), which did not condense in a trap cooled to −23°, distilled in a nitrogen atmosphere at 86° (757 mm.) and was identified as (1,1,1,3,3,3-hexafluoropropoxy)trimethylsilane.

One other fraction which condensed at −23° was isolated whose H^1 n.m.r. spectrum showed CH_3 absorptions at +0.02 and +0.14 p.p.m. and multiplets of seven peaks at −3.95 and −4.49 p.p.m. This spectrum could be duplicated by addition of hexafluoroacetone to excess propoxysilane. Upon addition of excess hexafluoroacetone the H^1 spectrum contained only one CH_3

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[2] See for example (a) D. Cook, *Can. J. Chem.*, **41**, 522 (1963); (b) M. F. Lappert, *J. Chem. Soc.*, 818 (1961); (c) P. N. Gates and E. E. Mooney, *ibid.*, 4648 (1964).

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TABLE I

SOME 1,1,1,3,3,3-HEXAFLUOROPROPOXY DERIVATIVES

	B.p.,	Carbon, %		Hydrogen, %		Fluorine, %	
Compound	°C. (mm.)	Calcd.	Found	Calcd.	Found	Calcd.	Found
$(CH_3)_3SiOCH(CF_3)_2$[a]	86 (757)	30.0	29.9	4.2	4.3	47.5	47.2
$(CH_3)_3GeOCH(CF_3)_2$[b]	117 (758)	25.4	25.3	3.7	3.6	...	...
$(CH_3)_3SnOCH(CF_3)_2$[b]	76 (58)	21.8	21.3	3.0	2.5	...	...
$(CH_3)_3SnOCH(CF_3)_2 \cdot (CF_3)_2CO$[c,d]	...[g]	21.7	21.9	2.0	2.2	46.0	45.5
$(CH_3)_2Sn[OCH(CF_3)_2]_2$[b]	92 (25)	19.9	20.1	1.7	1.7	...	...
$(CH_3)_2Sn[OCH(CF_3)_2]_2 \cdot 2(CF_3)_2CO$[b,e]	...	20.6	20.8	1.0	1.5	...	...
$(C_4H_9)_2Sn[OCH(CF_3)_2]_2$[c,f]	75 (10^{-3})	29.6	30.0	3.5	3.6	40.2	38.9

[a] Analysis by Alfred Bernhardt Mikroanalytisches Laboratorium, Mulheim (Ruhr), West Germany. [b] Analysis for C and H by Mrs. C. Jenkins, Chemistry Department, University of British Columbia, Vancouver, Canada. [c] Analysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [d] Calcd.: Sn, 23.9. Found: Sn, 23.8. [e] Hexafluoroacetone percentage was determined by quantitative reaction. Calcd.: 40.7. Found: 40.2. [f] Calcd.: Sn, 20.9. Found: Sn, 21.6. [g] Melting point in sealed tube is 23°.

TABLE II

SOME H^1 AND F^{19} CHEMICAL SHIFTS AND COUPLING CONSTANTS[a]

Compound	δCH_3,[b] p.p.m.	δH,[b,c] p.p.m.	J_{H-F},[d] c.p.s.	δF(propoxy),[e] p.p.m.	δF(ketone), p.p.m.
$(CH_3)_3SiOCH(CF_3)_2$	+0.16	−3.90	6.0	−0.65[f]	...
$(CH_3)_3SiOCH(CF_3)_2 \cdot (CF_3)_2CO$[g]	+0.08	−4.45	5.8	−2.51[h]	+5.09[h]
$(CH_3)_3GeOCH(CF_3)_2$	−0.25	−3.96	6.1	−1.65[f]	...
$(CH_3)_3GeOCH(CF_3)_2 \cdot (CF_3)_2CO$[g]	−0.27	−4.56	6.1	−2.9[h,j]	+3.4[h,j]
$(CH_3)_3SnOCH(CF_3)_2$	−0.38	−4.14	6.1	−1.7[f]	...
$(CH_3)_3SnOCH(CF_3)_2 \cdot (CF_3)_2CO$[g]	−0.27	−4.58	6.1	−3.1[h]	+4.4[h]
$(CH_3)_2Sn[OCH(CF_3)_2]_2$	−0.85	−4.57	6.2	−2.07[f,i]	...
$(CH_3)_2Sn[OCH(CF_3)_2]_2 \cdot 2(CF_3)_2CO$[g]	−1.03	−4.88	6.0	−2.94[h]	+4.36[h]

[a] Spectra run on neat liquids unless otherwise indicated. Negative values of δ are downfield. [b] With respect to external tetramethylsilane. [c] Septet. [d] From H^1 spectra. [e] Doublet, $J \approx 6$ c.p.s. [f] With respect to external trifluoroacetic acid. [g] Solution in hexafluoroacetone. [h] With respect to internal hexafluoroacetone. [i] Solution in CCl_4. [j] Septet, $J = 2.5$ c.p.s.

TABLE III

INFRARED SPECTRA OF 1,1,1,3,3,3-HEXAFLUOROPROPOXY DERIVATIVES[a]

$HOCH(CF_3)_2$[b]	$(CH_3)_3$-$SiOCH(CF_3)_2$	$(CH_3)_3$-$GeOCH(CF_3)_3$	$(CH_3)_3$-$SnOCH(CF_3)_2$
1380 s	1378 s	1374 s	1374 s
1308 s	1307 vs	1304 vs	1300 vs
1273 vs	1270 s	1275 s	1275 s
1207 vs	1232 } vs 1212 }	1217 vs[c]	1210 vs[c]
	1172 s	1153 s	1164 s
1112 vs	1111 s	1106 s	1101 s
685 m	685 m	685 m	683 m

[a] Vapor state, values in cm.$^{-1}$. [b] From ref. 1. [c] Broad.

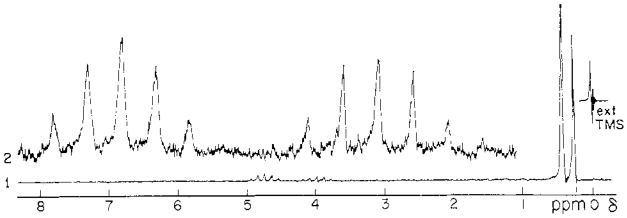


Figure 1.—H^1 n.m.r. spectrum of a mixture of $(CH_3)_3GeOCH(CF_3)_2$ and $(CH_3)_3GeOCH(CF_3)_2 \cdot (CF_3)_2CO$. The downfield proton region is expanded in curve 2.

peak at +0.08 p.p.m. and a multiplet at −4.45 p.p.m. (J = 5.8 c.p.s.). The F^{19} spectrum with excess hexafluoroacetone showed two peaks of equal area, in addition to the solvent peak.

It was established in another experiment done in an n.m.r. tube that reaction between the silane and the ketone occurs slowly at 20°, being complete after 17 hr.

(6) **Reaction of Trimethylgermane with Hexafluoroacetone.**—Trimethylgermane (6.35 g.) and the ketone (2.23 g.) were left at 20° for 15 hr. Trimethylgermane (4.80 g.) was recovered. The product (1,1,1,3,3,3-hexafluoropropoxy)trimethylgermane (3.81 g.) condensed in a trap cooled to −78°. The H^1 n.m.r. spectrum of a 2:1 mixture of the propoxygermane and hexafluoroacetone is shown in Figure 1, the two high-field peaks being centered at −0.43 and −0.27 p.p.m. and the lower field multiplets (seven peaks) at −4.74 and −3.98 p.p.m. The H^1 n.m.r. spectrum in excess hexafluoroacetone shows only one CH_3 peak at −0.27 p.p.m. and a single multiplet of seven peaks (J = 6.1 c.p.s.) at −4.56 p.p.m. The F^{19} spectrum of this solution shows two peaks of equal area in addition to that due to the solvent. The peaks are situated at −2.9 p.p.m. [doublet of septets (J = 6.0 and 2.5 c.p.s.)] and +3.4 p.p.m. (septet) relative to the hexafluoroacetone.

(7) **Reaction of Trimethyltin Chloride with Hexafluoroacetone.**—Trimethyltin chloride and excess hexafluoroacetone were immiscible at 20° and at temperatures up to 100°. Heating the mixture to 120° for 12 hr. caused no change.

Discussion

The addition of hexafluoroacetone to group IV hydrides to give 1,1,1,3,3,3-hexafluoropropoxy derivatives can be represented by the following equations (M = Si, Ge, Sn; R = CH_3, n-C_4H_9)

$$(CH_3)_3MH + (CF_3)_2CO \longrightarrow (CH_3)_3MOCH(CF_3)_2$$

$$R_2SnH_2 + 2(CF_3)_2CO \longrightarrow R_2Sn[OCH(CF_3)_2]_2$$

The direction of addition is thus the same as found by Parshall[5] for perfluorocyclobutanone reacting with di-n-butylsilane. The reaction of hexafluoroacetone with the tin hydrides is vigorous and exothermic but addition to the silane and germane is much slower. All reactions are quantitative. The products obtained in the present investigation are shown in Table I; their boiling points are in the range to be expected for such compounds. Their structure is best established by their n.m.r. spectra, Table II. The downfield proton peak split into a septet with $J \approx 6$ c.p.s. is convincing evidence for the group $-CH(CF_3)_2$ and this is confirmed by the doublet, $J \approx 6$ c.p.s., in the F^{19} spectra. The main bands in the infrared spectra of some of the propoxy compounds are shown in Table III, where they are compared with the corresponding bands of 1,1,1,3,3,3-hexafluoropropanol. The band at 685 cm.$^{-1}$ is assigned to a CF_3 deformation frequency and the others are probably due to C–F stretching. The similarity of the spectra is apparent. The spectrum of the propoxysilane also has a medium absorbance at 1071 cm.$^{-1}$ attributable to the Si–O–C asymmetric stretching vibration. Other bands due to vibrations such as C–H stretching and CH_3 rocking occur in the usual regions for these compounds and are not listed.

Tin hydrides usually reduce ketones to alcohols, being themselves oxidized to ditin compounds, and the suggested mechanism involves free radical attack by the hydride.[10] In the present investigation no reduction of the hexafluoroacetone was observed even in the presence of excess tin hydride.

To account for the direction of addition of the hexafluoroacetone to the group IV hydrides a reaction mechanism involving nucleophilic attack by the carbonyl oxygen on the central metal or metalloid atom is postulated. Thus a five-coordinated intermediate of the type $(CH_3)_3H\overset{-}{M}-O-\overset{+}{C}(CF_3)_2$ would be first formed followed by M–H cleavage induced by the carbonyl carbon from the same intermediate (most likely) or from a second intermediate.

Nucleophilic attack has often been suggested as the reaction route for compounds of silicon,[11] germanium,[11d,11e,12] and tin.[11e,13] In the present investigation some evidence that hexafluoroacetone could form the necessary intermediate comes from the result that the ketone forms complexes with the propoxy derivative as follows (M = Si, Ge, Sn)

$$(CH_3)_3MOCH(CF_3)_2 + (CF_3)_2CO \rightleftharpoons (CH_3)_3MOCH(CF_3)_2\cdot(CF_3)_2CO$$

$$(CH_3)_2Sn[OCH(CF_3)_2]_2 + 2(CF_3)_2CO \longrightarrow (CH_3)_2Sn[OCH(CF_3)_2]_2\cdot 2(CF_3)_2CO$$

For silicon and germanium this 1:1 complex readily dissociates at 20°, but for tin both complexes can be isolated, Table I. N.m.r. data for the complexes are given in Table II, and the H^1 spectrum of a mixture of the propoxygermane and its complex is shown in Figure 1. The spectrum was run on a solution of the propoxygermane in hexafluoroacetone (2:1 molar ratio). In excess hexafluoroacetone the spectrum consists of only one septet and one methyl peak. The spectra of the propoxysilane and its complex show similar features. In hexafluoroacetone the trimethyltin compound and its complex have different chemical shifts for the downfield proton but the methyl groups have the same chemical shifts. The stoichiometry of the complexes follows from the analysis of the compounds $(CH_3)_3SnOCH(CF_3)_2\cdot(CF_3)_2CO$ and $(CH_3)_2Sn[OCH(CF_3)_2]_2\cdot 2(CF_3)_2CO$, Table I, and from the equal areas of the peaks in the F^{19} spectra associated with the $-CH(CF_3)_2$ groups and the complexed hexafluoroacetone.

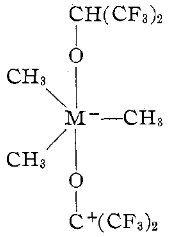
Trifluoroacetone does not complex with hexafluoropropoxytrimethyltin and hexafluoroacetone does not complex with trimethyltin chloride. The result with the tin chloride is particularly surprising in view of its well-known ability to form complexes.[14] The 1:1 complex, $(CH_3)_3SnOCH(CF_3)_2\cdot(CF_3)_2CO$, reacts immediately with trimethyltin hydride to form the uncomplexed propoxytin compound

$$(CH_3)_3SnH + (CH_3)_3SnOCH(CF_3)_2\cdot(CF_3)_2CO \longrightarrow 2(CH_3)_3SnOCH(CF_3)_2$$

It was also found that mixing bis(hexafluoropropoxy)-dimethyltin with its 1:2 complex, $(CH_3)_2Sn[OCH(CF_3)_2]_2\cdot 2(CF_3)_2CO$, yields a new compound which is apparently in equilibrium with the reactants. This new compound is believed to be the 1:1 complex, $(CH_3)_2Sn[OCH(CF_3)_2]_2\cdot(CF_3)_2CO$, formed by the reaction[15]

$$(CH_3)_2Sn[OCH(CF_3)_2]_2 + (CH_3)_2Sn[OCH(CF_3)_2]_2\cdot 2(CF_3)_2CO \rightleftharpoons 2(CH_3)_2Sn[OCH(CF_3)_2]_2\cdot(CF_3)_2CO$$

As mentioned in the introduction carbonyl compounds form complexes with Lewis acids, and it is established that bonding occurs through the oxygen atom of the carbonyl group.[2,3] The infrared spectra of the two tin complexes actually isolated in the present investi-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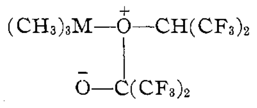
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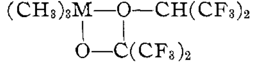
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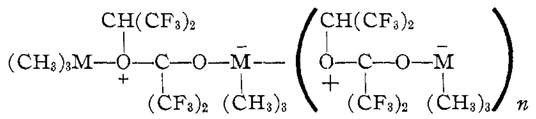
V

$$(CH_3)_3M-O-C(CF_3)_2-OCH(CF_3)_2$$
VI

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[15] An approximate equilibrium constant of 4.5 ± 2 can be calculated for this reaction if the relative intensities of the methyl absorptions in the H spectra are used as a measure of the concentration of the three species.

gation show no carbonyl absorption, the spectra being clear above 1375 cm.$^{-1}$ except for C–H stretching bands. Therefore in discussing the structures of the 1:1 complexes it seems that five alternatives, II–VI (M = Si, Ge, Sn), need to be considered. Structures II, IV, and V involve five-coordinated group IV atoms. In the organometallic field such coordination is well established for tin[14a,16] and silicon compounds,[17] although it seems to be unknown for germanium. Structure VI must be considered because it has recently been found[18] that aldehydes add reversibly to Sn–O bonds, *e.g.*

$$(C_4H_9)_3SnOCH_3 + RCHO \rightleftharpoons (C_4H_9)_3Sn—O—CHR—OCH_3$$

and apparently similar reactions occur with ketones.[19] Such addition would probably occur through intermediates of structure IV. Structure III is suggested because of the strong electrophilic nature of the carbon atom of the carbonyl group of hexafluoroacetone.[3] However, the oxygen atom in III with its negative charge should be an even better electron donor than in the free ketone. Thus III would be expected to be unstable with respect to IV or V. Structures II, V, and VI are supported by the H^1 n.m.r. spectra of the complexes, which show that the three methyl groups in a given compound have the same chemical shift. However, this does not exclude IV since the differences in chemical shifts expected for the three methyl groups may be too small to be detected. The bulk of n.m.r. evidence suggests that II is not the structure. First, in IV and V the resonance due to the proton of the $-CH(CF_3)_2$ group would be expected to be downfield from that in the uncomplexed propoxy derivative because of the positive charge on the adjacent oxygen. This is found, as can be seen in Table II and Figure 1. The electronegative CF_3 groups of the inserted ketone in VI could also cause a simliar effect, although this might be expected to be less pronounced. The same proton in II would be expected to be found upfield from the uncomplexed compound because of the negative charge on the central atom. Second, the fluorine resonance due to the complexed ketone in II would be expected to be downfield from that of hexafluoroacetone because of the greater positive charge on the carbon atom. However, the resonance is in fact upfield from hexafluoroacetone. Third, the peaks in the F^{19} spectra of the germanium complex are split into septets (J = 2.5 c.p.s.), which strongly suggests fluorine–fluorine coupling is present. This could occur "through space,"[20] through six bonds (as in IV, V, and VI), or through eight bonds (as in II). The magnitude of the coupling constant seems to favor coupling "through space"[21] or through six bonds.[22]

The methyl groups in the propoxy compounds $(CH_3)_3MOCH(CF_3)_2$ are in essentially the same environment as in VI and consequently very little change in chemical shift of the methyl protons would be expected on going from one to the other. As is seen in Figure 1 there is a significant difference in this chemical shift for the two germanium compounds in hexafluoroacetone solution and the same is true for the silicon derivatives. However, the tin compounds have the same chemical shift in hexafluoroacetone solution. These results suggest that whereas VI is likely for the tin complex IV or V are more likely when M = Ge or Si. In the case of the solid tin complex an X-ray study is planned in an attempt to resolve the problem.[23]

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(21) The idea of through space coupling has been questioned recently by K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1339 (1965).

(22) Coupling through eight bonds would also involve coupling through one germanium and two oxygen atoms and thus would be expected to be very small.

(23) Note Added in Proof.—It has been found by A. F. Janzen and C. J. Willis (*Can. J. Chem.*, in press) that methylsilane, dimethylsilane, and trichlorosilane add to hexafluoroacetone on ultraviolet irradiation. At −78° trimethylsilane and hexafluoroacetone give the propoxysilane, $(CH_3)_3SiOCH(CF_3)_2$, described above, together with a low yield of the compound $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$ which apparently is not the same as the 1:1 complex described above.