R. Muller, Organofluorosilicate Chemistry in "Silicon Compounds: Register and Review (3rd edition – S-6), B. Arkles, R. Anderson, G.L. Larson eds. 50-59, 1984

Organofluorosilicate Chemistry

*Richard Müller**

Organofluorosilicates (OFS) can be easily prepared both in water and in organic fluids and handled without danger. They readily react likewise both in water and also in organic fluids mostly at room temperature although they are soluble only in the first but not in organic fluids. From them it is possible to prepare metal organic compounds of Ag (Au, Cu), Hg, Pb, Sb, Bi, Co, Tl, and Pd. Alkanes, alkenes, dienes, aromatics, biaromatics, halocarbons, alcohols, aldehydes, esters, ethers, pseudohalocarbons and tetracyanocarbons can also be prepared. They are a new class of compounds widely applicable to syntheses. It is the intention to show this in the following report.

Preparation and properties of the OFS

Organopentafluorosilicates (OPFS)

Preparation in water

Booth and coworkers [1], [2] tried to prepare OPFSs by passing $C_2H_5SiF_3$ over NaF without success. Tansjö [3] obtained OPFSs by treating phenyltriaminosilanes ($C_6H_5Si(NHR)_3$) with anhydrous hydrogen fluoride in ether. He more accurately and unambiguously described them first in 1964 [4], [5], although he did not perceive their astonishing properties.
We have utilized the solubility and stability of the $RSiF_3$ compounds in H_2O and have added them to solutions of alkali fluorides in H_2O. In this manner solutions of the OPFSs are obtained [6].

$$RSiF_3 + 2\,MF \xrightarrow{H_2O} M_2[RSiF_5] \qquad (1)$$

---

* Formerly Director of the Institut für Silikon- und Fluorkarbonchemie, Radebeul-Dresden

$R=CH_3—,\quad C_2H_5—,\quad n\text{-}C_3H_7—,\quad CH_2=CH—,\quad CH_3CH=CH—,$
$CH_2=CHCH_2—,\ C_6H_5—,\ CF_2=CF—\ etc.$
$M=NH_4—,\ Na—,\ K—,\ Rb—,\ Cs—,\ RNH_3—\ etc.$
The OPFS solubilities are shown in Table 1 [7], [8], [9].

If the concentration is higher than the saturation the OPFSs precipitate and can be isolated in the solid state. The solubility decreases if an excess of MF exists. But in such cases double salts precipitate too, for instance $(NH_4)_2[CH_3SiF_5]\cdot NH_4F$ or $(NH_4)_2[F_5SiCH_2=CHCH=CH_2SiF_5]\cdot 2\,NH_4F$ [9], [10], [11], [12]. These are not mixtures as shown by x-ray pictures [9]. The OPFS are not soluble in all organic fluids. Exceptions are $Rb_2[n\text{-}C_8H_{17}SiF_5]$ and $Cs_2[n\text{-}C_8H_{17}SiF_5]$. They are slightly soluble in ethanol from which they can be recrystallized [10]. Because of this insolubility they can also be precipitated from aqueous solution, e.g. with C_2H_5OH [7]. OPFSs which are readily soluble in H_2O can be transformed into slightly soluble OPFSs by exchanging the cation (cf. tab. 1)

$$(NH_4)_2[C_2H_5SiF_5] + 2\,KCl \rightarrow K_2[C_2H_5SiF_5] + 2\,NH_4Cl \qquad (2)$$
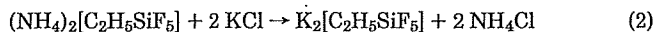
The solubility of the OPFSs in H_2O does not solely depend on the counter cation (e.g. K, Na, NH_4) but also on the organic group. If its size increases the solubility decreases. The different solubility in H_2O and in organic fluids can perhaps be used to separate, to enrich or possibly even to analyse the alkali metals by varying R.

All substituents or groups X on a trifunctional silicon which are hydrolysable can be exchanged for fluorine in aqueous solution:
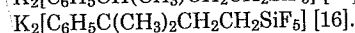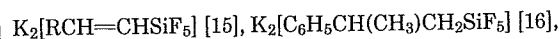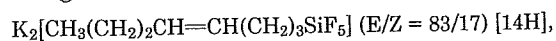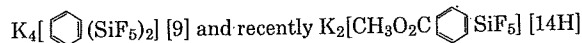
$$RSiX_3 + 5\,NaF \xrightarrow{H_2O} Na_2[RSiF_5] + 3\,NaX \qquad (3)$$
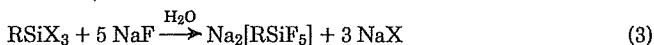
X = Cl, Br, I, RCOO, OH, OR and so on.

Tab. 1 The solubility of the OPFSs in H_2O at room temperature

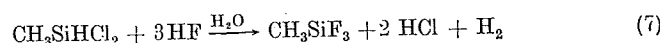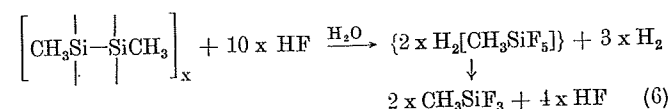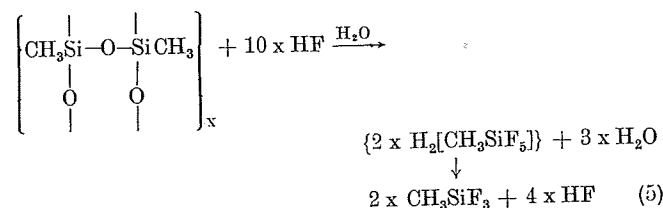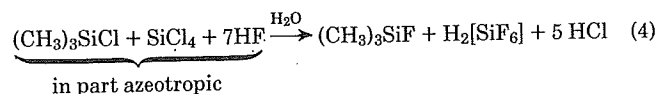| OPFS	Solubility g/100 g H_2O	OPFS	Solubility g/100 g H_2O
$(NH_4)_2[CH_3SiF_5]$	67	$Rb_2[CH_3SiF_5]$	5
$(NH_4)_2[C_2H_5SiF_5]$	122	$Cs_2[CH_3SiF_5]$	100
$(NH_4)_2[n\text{-}C_3H_7SiF_5]$	67	$Na_2[CH=CHSiF_5]$	6,6
$Na_2[CH_3SiF_5]$	3	$(NH_4)_2[C_{12}H_{25}SiF_5]$	unstable in H_2O
$K_2[C_2H_5SiF_5]$	3	$K_2[CH_2=CHSiF_5]$	1,5
$Na_2[n\text{-}C_3H_7SiF_5]$		$(NH_4)_2[C_6H_5SiF_5]$	43
$K_2[CH_3SiF_5]$	1,5	$Na_2[C_6H_5SiF_5]$	1,9
$(NH_4)_2[CH_2=CHSiF_5]$	slightly soluble	$K_2[C_6H_5SiF_5]$	0,4
$K_2[n\text{-}C_3H_7SiF_5]$		$(C_6H_5NH_3)_2[CH_3SiF_5]$	
$(NH_4)_2[CH_2=CHCH_2SiF_5]$			
$(NH_4)_2[CH_3CH=CHSiF_5]$	*		

* in accordance with the color test (see below) preparable but not separable. $CH_3CH=CH_2$ is eliminated [7], [10] (see (47))

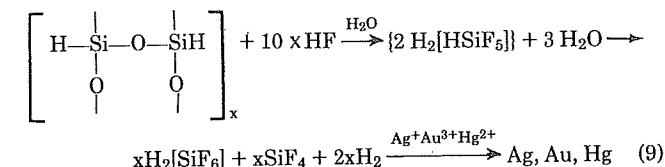The methods can be applied to different R groups. For instance the following compounds have also been prepared in H_2O:

$K_4[\bigcirc(SiF_5)_2]$ [9] and recently $K_2[CH_3O_2C\bigcirc SiF_5]$ [14H]

$K_2[CH_3(CH_2)_2CH=CH(CH_2)_3SiF_5]$ (E/Z = 83/17) [14H],

$K_2[RCH=CHSiF_5]$ [15], $K_2[C_6H_5CH(CH_3)CH_2SiF_5]$ [16],

$K_2[C_6H_5CH(CH_3)CH_2CH_2SiF_5]$ [16] and
$K_2[C_6H_5C(CH_3)_2CH_2CH_2SiF_5]$ [16].

Mono- (R_3SiX) and bifunctional (R_2SiX_2) organofluorosilanes do not react under these conditions to form stable OFSs (but see below!) Therefore it is possible to separate e.g. the CH_3SiCl_3 from the other products of the "direct synthesis" between Si and CH_3Cl in the form of $(NH_4)_2[CH_3SiF_5]$ by transforming the methylchlorosilanes to the methylfluorosilanes with aqueous HF [6], [9], [11], [13]. The mixture which principally consists of $(CH_3)_3SiF$, $(CH_3)_2SiF_2$ and CH_3SiF_3 passes through an aqueous NH_4F solution. The CH_3SiF_3 precipitates in the form of $(NH_4)_2[CH_3SiF_5]$ and can be filtered off. $(CH_3)_3SiF$ and $(CH_3)_2SiF_2$ remain gaseous. Their boiling points are widely separated and can be easily separated by distillation (see Fig. 1). The methyl-PFS is finally decomposed with acid and the CH_3SiF_3 can be recovered in this manner.

Moreover the following reactions can be run with the other products from the "direct synthesis":

$$\underbrace{(CH_3)_3SiCl + SiCl_4 + 7HF}_{\text{in part azeotropic}} \xrightarrow{H_2O} (CH_3)_3SiF + H_2[SiF_6] + 5\,HCl \quad (4)$$

$$\begin{bmatrix} CH_3\overset{|}{\underset{O|}{Si}}{-}O{-}\overset{|}{\underset{O|}{Si}}CH_3 \end{bmatrix}_x + 10\,x\,HF \xrightarrow{H_2O}$$
$$\{2\,x\,H_2[CH_3SiF_5]\} + 3\,x\,H_2O$$
$$\downarrow$$
$$2\,x\,CH_3SiF_3 + 4\,x\,HF \quad (5)$$

$$\begin{bmatrix} CH_3\overset{|}{\underset{|}{Si}}{-}\overset{|}{\underset{|}{Si}}CH_3 \end{bmatrix}_x + 10\,x\,HF \xrightarrow{H_2O} \{2\,x\,H_2[CH_3SiF_5]\} + 3\,x\,H_2$$
$$\downarrow$$
$$2\,x\,CH_3SiF_3 + 4\,x\,HF \quad (6)$$

$$CH_3SiHCl_2 + 3HF \xrightarrow{H_2O} CH_3SiF_3 + 2\,HCl + H_2 \quad (7)$$

$$2HSiCl_3 + 10HF \xrightarrow{H_2O} \{2\,H_2[HSiF_5]\} + 6HCl \quad (8)$$
$$\downarrow$$
$$H_2SiF_6 + SiF_4 + 6HCl + 2H_2$$
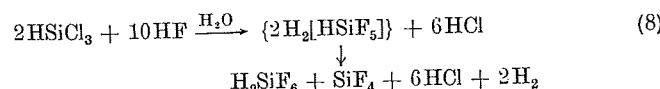
The salts of this acid ($M_2[HSiF_5]$) form white precipitates which decompose spontaneously. Another earlier observation elucidated the existence of this acid. The reductions of Ag-, Au- and Hg-salts by the

polymeric disiloxane are accelerated in the presence of fluoride ions: [17]

$$\begin{bmatrix} H{-}\overset{|}{\underset{O|}{Si}}{-}O{-}\overset{|}{\underset{O|}{Si}}H \end{bmatrix}_x + 10\,x\,HF \xrightarrow{H_2O} \{2\,H_2[HSiF_5]\} + 3\,H_2O \longrightarrow$$
$$xH_2[SiF_6] + xSiF_4 + 2xH_2 \xrightarrow{Ag^+Au^{3+}Hg^{2+}} Ag, Au, Hg \quad (9)$$

Furthermore, whilst $HSiCl_3$, $HSiBr_3$ and $HSiI_3$ hydrolyse to polymeric disiloxane the different behavior of $HSiF_3$ is probably based on the formation of the acid:
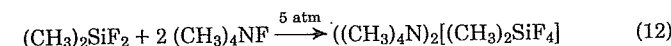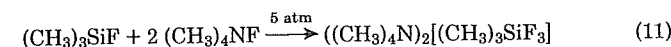
$$2\,HSiF_3 + 3H_2O \rightarrow \underbrace{\{H_2[HSiF_5]\} + HF}_{H_2[SiF_6] + H_2} + H_2SiO_3 + H_2 \quad (10)$$
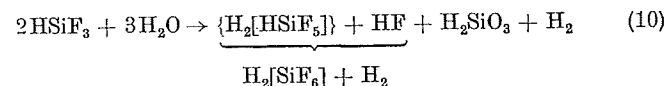
Pyrolysis [8]
$Na_2[CH_3SiF_5]$ gave 95% CH_3SiF_3 on heating. $(NH_4)_2[CH_3SiF_5]$ decomposed CH_4, NH_3 and the adduct $CH_3SiF_3 \cdot NH_3$. $K_2[CH_3SiF_5]$ was converted to carbon and hydrocarbons.

Electrolysis [13]
Electrolysis between Pt electrodes in aqueous solutions gave CH_4 and C_2H_6 from $M_2[CH_3SiF_5]$ and C_6H_6 from $M_2[C_6H_5SiF_5]$.

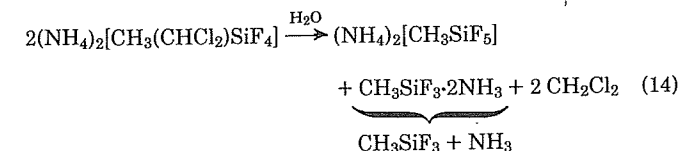### Organotri- and organotetrafluorosilicates

Using the conditions of fig. 1 the mono- and bifunctional fluorosilanes did not form OFSs. OFSs with hexacoordinated silicon could be prepared under pressure: [18]

$$(CH_3)_3SiF + 2\,(CH_3)_4NF \xrightarrow{5\,atm} ((CH_3)_4N)_2[(CH_3)_3SiF_3] \quad (11)$$

$$(CH_3)_2SiF_2 + 2\,(CH_3)_4NF \xrightarrow{5\,atm} ((CH_3)_4N)_2[(CH_3)_2SiF_4] \quad (12)$$

In order to enhance the negativity of the methyl group we substituted halogens. We presumed that it could be possible to prepare OFSs from bifunctional organofluorosilanes without pressure. $CH_3(CH_2Cl)SiCl_2$ and $CH_3(CH_2Br)SiCl_2$ were not suitable but the following reaction occurred: [19]

$$CH_3(CHCl_2)SiF_2 + 2\,NH_4F \xrightarrow[<30°C]{H_2O} (NH_4)_2[CH_3(CHCl_2)SiF_4] \quad (13)$$
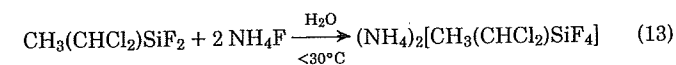
However, the compound was unstable in water and gradually decomposed in the following manner:

$$2(NH_4)_2[CH_3(CHCl_2)SiF_4] \xrightarrow{H_2O} (NH_4)_2[CH_3SiF_5]$$
$$+ \underbrace{CH_3SiF_3 \cdot 2NH_3}_{CH_3SiF_3 + NH_3} + 2\,CH_2Cl_2 \quad (14)$$

The diphenyltetrafluorosilicate with hexacoordinated Si which was obtained from $(C_6H_5)_2SiF_2$ with primary ammonium fluorides was transformed to the OPFS during the preparation [4], [5], [9]

$$(RNH_3)_2[(C_6H_5)_2SiF_4] + RNH_3F$$
$$\xrightarrow{H_2O} (RNH_3)_2[C_6H_5SiF_5] + C_6H_6 + RNH_2 \quad (15)$$
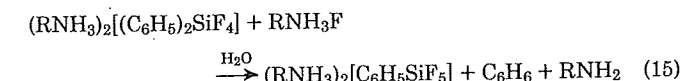
Quarternary ammonium fluorides provided OFSs with pentacoordinated Si from trifluorosilanes: [13], [20], [21]

$$(C_2H_5)_4NF + CH_3SiF_3 \xrightarrow[(C_6H_5OH)]{H_2O} (C_2H_5)_4N[CH_3SiF_4] \quad (16)$$
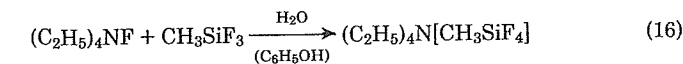
In contrast to the OPFSs the organotetrafluorosilicate was soluble in ethanol and could be recrystallized from it.
In the same manner $(n-C_3H_7)_4N[C_6H_5SiF_4]$ and $(n-C_3H_7)_2NH_2[C_6H_5SiF_4]$ were obtained.
From $(CH_3)_2SiF_2$ a dimethyltrifluorosilicate could be prepared:

$$(C_2H_5)_4NF + (CH_3)_2SiF_2 \rightarrow (C_2H_5)_4N[(CH_3)_2SiF_3] \quad (17)$$

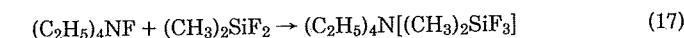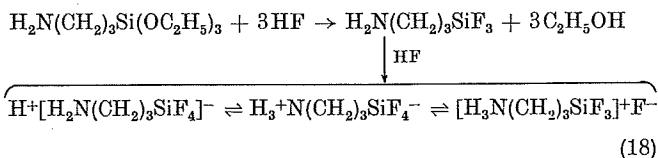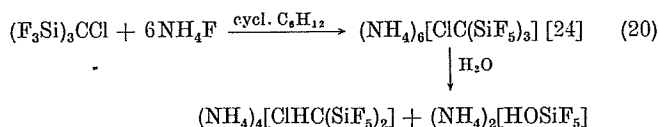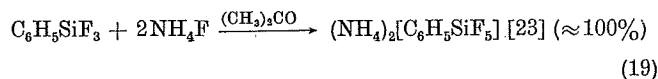| b.p. °C	%		b.p./°C
31,8	0,1	HSiCl₃	
40,4	1,0	CH₃HSiCl₂	
57,3	0,2	SiCl₄	
57,6	5,1	(CH₃)₃SiCl	
72,6	63,5	(CH₃)₂SiCl₂	
66,1	22,8	CH₃SiCl₃	
>72	5,0	Chlor-polysiloxane / Chlor-polysilane	
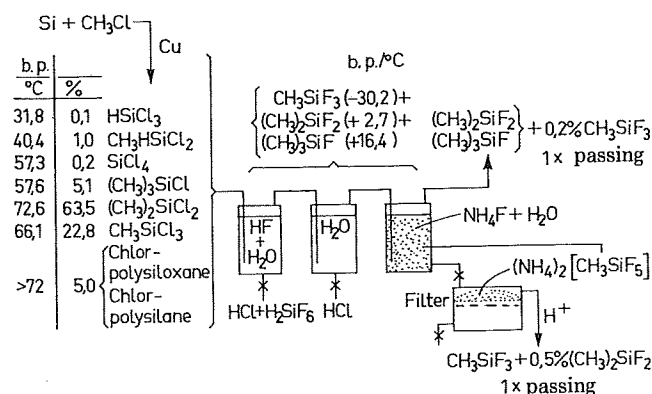
Fig. 1.

Finally it was recently proved that R_3SiF and R_2SiF_2 can form short lived OFSs, respectively, with a catalytic or excess amount of KF and that all their R-groups can be split off [22].

By forming an amphoteric ion acids of the OFSs with pentacoordinated Si can be stabilized by insertion of NH_2-groups into R [9].

$$H_2N(CH_2)_3Si(OC_2H_5)_3 + 3\,HF \rightarrow H_2N(CH_2)_3SiF_3 + 3\,C_2H_5OH$$

$$\downarrow HF$$

$$H^+[H_2N(CH_2)_3SiF_4]^- \rightleftharpoons H_3^+N(CH_2)_3SiF_4^- \rightleftharpoons [H_3N(CH_2)_3SiF_3]^+F^-$$

(18)

Crystallization from hot water gave large crystals. $H_2^+[H_2N(CH_3)_2NH(CH_2)_3SiF_5]^{2-}$ was prepared in the same manner.
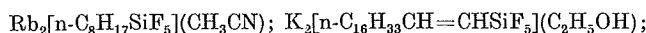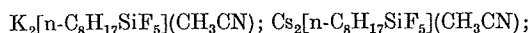
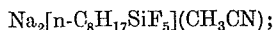*Preparation of OPFSs in organic fluids*

OPFSs can be prepared in organic fluids.

$$C_6H_5SiF_3 + 2\,NH_4F \xrightarrow{(CH_3)_2CO} (NH_4)_2[C_6H_5SiF_5]\ [23]\ (\approx 100\%)$$

(19)

$$(F_3Si)_3CCl + 6\,NH_4F \xrightarrow{cycl.\ C_6H_{12}} (NH_4)_6[ClC(SiF_5)_3]\ [24]$$

(20)

$$\downarrow H_2O$$

$$(NH_4)_4[ClHC(SiF_5)_2] + (NH_4)_2[HOSiF_5]$$

In organic fluids were also obtained: $(NH_4)_2[CH_3SiF_5]((CH_3)_2CO)$ [23]; $(NH_4)_2[ClH_2CSiF_5](CH_3CN)$; $(NH_4)_4[Cl_2C(SiF_5)_2](CH_3CN)$; $(NH_4)_4[CH_2(SiF_5)_2](CCl_4)$ [24]; $K_2[CF_2=CFSiF_5](CH_3CN$ or Dioxan); $Na_2[CF_2=CFSiF_5](CH_3CN$ or Dioxan) [25].

Recently the following OPFSs were prepared in this manner:

$$K_2\left[\begin{array}{c}\text{(tetralin-SiF}_5)\end{array}\right](C_2H_5OH)\ [14h],\ [16];\quad K_2\left[\begin{array}{c}\text{(norbornane-SiF}_5)\end{array}\right](C_2H_5OH)\ [14g],$$

$$K_2\left[CH_3(CH_2)_3{-}C{=}C\underset{H}{\overset{(CH_2)_3CH_3}{<}}\underset{SiF_5}{}\right](C_2H_5OH);\ [15]$$

$Na_2[n\text{-}C_8H_{17}SiF_5](CH_3CN)$;

$K_2[n\text{-}C_8H_{17}SiF_5](CH_3CN)$; $Cs_2[n\text{-}C_8H_{17}SiF_5](CH_3CN)$;

$Rb_2[n\text{-}C_8H_{17}SiF_5](CH_3CN)$; $K_2[n\text{-}C_{16}H_{33}CH{=}CHSiF_5](C_2H_5OH)$;

$K_2[n\text{-}C_{18}H_{37}SiF_5](C_2H_5OH)$; $K_2[C_6H_5CH{=}CHSiF_5](C_2H_5OH)$;

$K_2[n\text{-}C_{16}H_{33}CH{=}CHSiF_5](C_2H_5OH)$;

$K_2[CH_3(CH_2)_6CH{=}CH(CH_2)_6CH_2SiF_5](C_2H_5OH)$ [10].
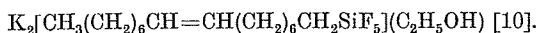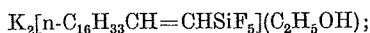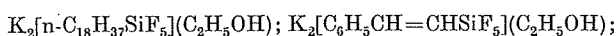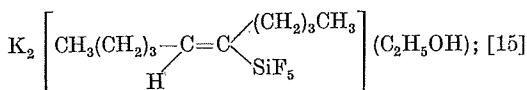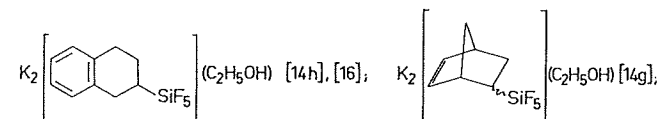
Preparation of the OPFSs without solvent

The intention of Booth and coworkers (see above!) could be realized by exchanging the NaF for KF and the $C_2H_5SiF_3$ for CH_3SiF_3 [6]:

$$CH_3SiF_3 + 2\,KF(solid) \xrightarrow{\sim20°C} K_2[CH_3SiF_5]$$

(21)
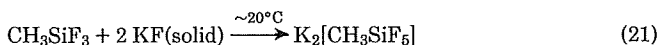
The hexa- and pentacoordination of the Si in the OFSs could be demonstrated spectroscopically [21], [26–29]. (IR-spectra see [9], [13A]!)

Syntheses with OPFSs

Syntheses in H_2O

Syntheses of metal-organic compounds

Ag: If $AgNO_3$ or AgF are reacted with aqueous OPFSs an intensive color develops followed quickly by precipitation of a colored sediment [6], [9], [11], [13] (see tab. 2) corresponding to the bright yellow $(C_6H_5Ag)_2\cdot AgNO_3$ which has been prepared from $(C_6H_5)_3C_2H_5Pb$ or $(C_6H_5)_3C_2H_5Sn$ in anhydrous ethanol by Krause and Schmitz [30].

These compounds decompose in H_2O rapidly to metallic Ag and coupled (C_2H_6, $CH_2{=}CHCH{=}CH_2$, $(C_6H_5)_2$) and protonolysis-products (CH_4, $CH{=}CH_2$, C_6H_6). The precipitates could not be studied in detail because of this rapid decomposition. They show a tendency to "explode" on the filter.
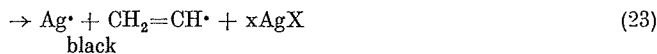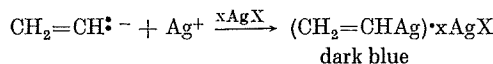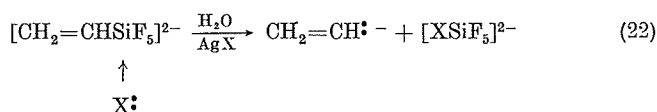
Tab. 2 Color-test with AgF or $AgNO_3$ in H_2O

| R in [RSiF_5]	color	R—R (%)	R—H (%)
CH_3—	yellow a)	85–93	15 – 7
$CH_2{=}CH$—	dark blue b)	87,1	
$CH_3CH{=}CH$—	blue		
$CH_2{=}CHCH_2$—	red purple		
C_6H_5—	yellow-orange		
(o-tolyl)	yellow-orange		

a) fire-like decomposition by heating

b) with excess $AgNO_3$ the color changes via green to yellow

In some cases the protonolysis predominates; the color-test is then hindered. Its rate depends on R. The larger is R the slower the rate. For instance the color of $(NH_4)_2[n\text{-}C_{12}H_{25}SiF_5]$ is slow to form. (Color test in organic fluids see table 3!)

The following reactions evidently occur in H_2O:

$$[CH_2{=}CHSiF_5]^{2-} \xrightarrow[AgX]{H_2O} CH_2{=}CH^{\bullet\,-} + [XSiF_5]^{2-}$$

(22)

$$\uparrow$$

$$X^{\bullet}$$

$$CH_2{=}CH^{\bullet\,-} + Ag^+ \xrightarrow{xAgX} (CH_2{=}CHAg)\cdot xAgX$$

$$\text{dark blue}$$

$$\rightarrow Ag^\bullet + CH_2{=}CH^\bullet + xAgX$$

$$\text{black}$$

(23)

Homocoupling: $2\,CH_2{=}CH^\bullet \rightarrow CH_2{=}CHCH{=}CH_2$ (24)

Protonolysis without significant formation of Ag or Ag_2O was observed:

$$2[RSiF_5]^{2-} + 3\,H_2O \xrightarrow{Ag^+} 2\,RH + [SiF_6]^{2-} + H_2SiO_3 + 2\,HF_2^-$$

(25)
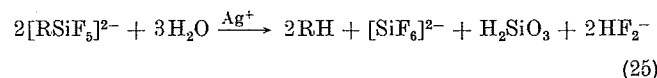
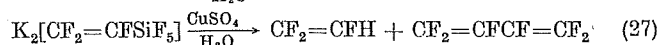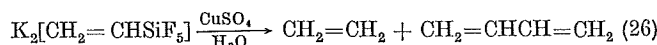With Ag-salts $[CF_2{=}CFSiF_5]^{2-}$ gave only $CF_2{=}CFH$ both in H_2O and ethanol [25] (cf. (26)!)

Corresponding to (2) the siliconates, e.g. $Na(OH)_2SiCH{=}CH_2$, the silantriols, e.g. $CH_2{=}CHSi(OH_3)$, the silatranes, e.g.

$$CH_2{=}CHSi(\overline{OCH_2CH_2})_3N,$$ the bis(acetylacetonyl)organosilicon

chlorides, e.g.
$$\left(\begin{array}{c}CH_3\\HC{<}^{C-O}_{C=O}\\CH_2\end{array}\right)_2>Si(CH{=}CH_2)Cl\ [6],$$
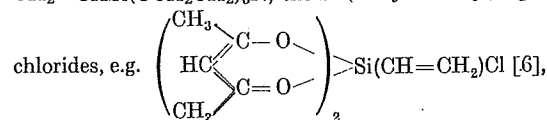
and the organotetrafluorosilicates [20], e.g. $(C_2H_5)_4N[CH_3SiF_4]$, gave likewise the color-test with Ag-salts but only in the presence of added MF. These results are worthy of notice because the silicons with the higher coordination exist in the anion and the cation or in a neutral molecule.

Cu: The OPFSs can also be decomposed by Cu-salts. Both protonolysis- and homocoupling-products, diene, are formed:

$$K_2[CH_2{=}CHSiF_5] \xrightarrow{CuSO_4}_{H_2O} CH_2{=}CH_2 + CH_2{=}CHCH{=}CH_2$$ (26)

$$K_2[CF_2{=}CFSiF_5] \xrightarrow{CuSO_4}_{H_2O} CF_2{=}CFH + CF_2{=}CFCF{=}CF_2$$ (27)

(cf. above!) [7] [25]

The formation of organocopper intermediates is probable but it could not be proved.

The R of the OPFSs can be added to the double bond of unsaturated α,β-ketones with $Cu(OAc)_2$ in the presence of water: [14F], [45]

$K_2[n\text{-}C_8H_{17}SiF_5] + CH_2{=}CHC(O)CH_3 + H_2O$

$\xrightarrow[\Delta\ 135°C]{Cu(OAc)_2} n\text{-}C_8H_{17}(CH_2)_2C(O)CH_3 + K_2[HOSiF_5]$ (28)
(70%)
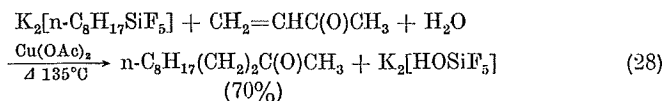
In this manner n-C$_8$H$_{17}$—⬡=O (16%) and

$CH_3O_2C(CH_2)_{10}(CH_2)_2C(O)CH_3$ (46%) could be prepared.

With alkenyl-PFSs and solid CuCl the following reaction occurred: [14], [31]

$K_2[R^1CH{=}CR^2SiF_5] \xrightarrow[3-20\ mm\ Hg]{CuCl\ 200-300°C}$

$\begin{matrix}R^1\\H\end{matrix}{>}C{=}C{<}\begin{matrix}R^2\\ \end{matrix}C{=}C{<}\begin{matrix}H\\R^1\end{matrix}$ $\begin{matrix} \\R^2\end{matrix}$

(E, E)-1,3-Diene

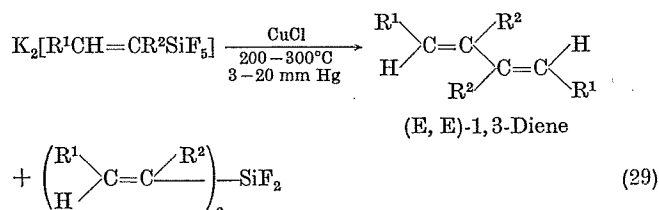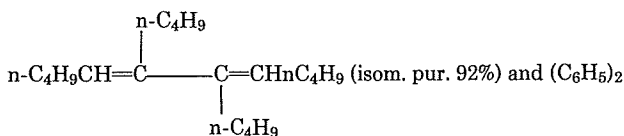$+ \left(\begin{matrix}R^1\\H\end{matrix}{>}C{=}C{<}\begin{matrix}R^2\\ \end{matrix}\right)_2{-}SiF_2$ (29)

(E,E)-7,9-hexadecadiene (56%, isomeric purity 95%) and dioctenyldifluorosilane (8%) were likewise produced from (E)-1-octenyl-PFS. Also the (E,E)-n-C$_4$H$_9$CH=CHCH=CHC$_4$H$_9$-n (isom. pur. 96%), (E,E)-CH$_3$OCH$_2$CH=CHCH=CHCH$_2$OCH$_3$ (isom. pur. 97%), (E,E)-C$_6$H$_5$CH=CHCH=CHC$_6$H$_5$ (isom. pur. 99%),

n-C$_4$H$_9$CH=C(—n-C$_4$H$_9$)—C(—n-C$_4$H$_9$)=CHnC$_4$H$_9$ (isom. pur. 92%) and (C$_6$H$_5$)$_2$
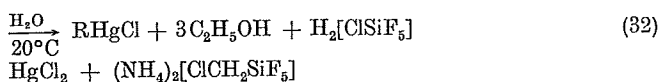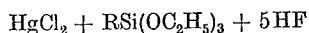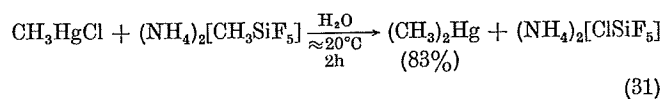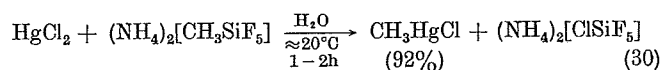
were obtained.

In contrast to these reactions solid CuCl gave with alkyl-OFSs under these conditions only protonolysis products and (by β-elimination) olefins and no homocoupling products.
Solid CuF$_2$·2H$_2$O produced almost entirely protonolysis products in this manner. As for the mechanism the formation of organocopper(II) intermediates and of radical ions is proposed (see (71)!)

Au: HAuCl$_4$·4H$_2$O is soluble both in H$_2$O, ethanol, and ether and therefore especially favourable for comparative studies. Nevertheless we could not study the dark colored precipitates which it gives with the OPFSs in H$_2$O more accurately. The decomposition products are unknown [8].
Stable metal organic compounds could be obtained from the following elements:
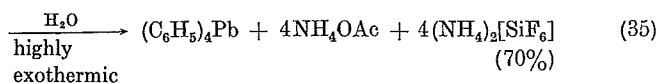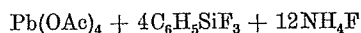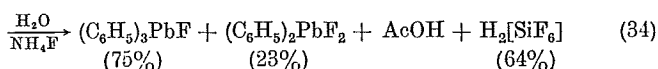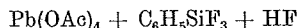
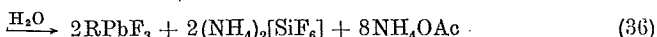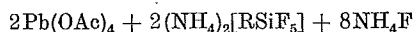Hg: With Hg(II) salts and OPFSs the following reactions occurred: [6], [32]

$HgCl_2 + (NH_4)_2[CH_3SiF_5] \xrightarrow[1-2h]{H_2O\ \approx20°C} CH_3HgCl + (NH_4)_2[ClSiF_5]$ (30)
(92%)

$CH_3HgCl + (NH_4)_2[CH_3SiF_5] \xrightarrow[2h]{H_2O\ \approx20°C} (CH_3)_2Hg + (NH_4)_2[ClSiF_5]$ (31)
(83%)

$HgCl_2 + RSi(OC_2H_5)_3 + 5HF$

$\xrightarrow[20°C]{H_2O} RHgCl + 3C_2H_5OH + H_2[ClSiF_5]$ (32)

$HgCl_2 + (NH_4)_2[ClCH_2SiF_5]$

$\xrightarrow{H_2O} ClCH_2HgCl + (NH_4)_2[ClSiF_5]$ [24] (33)
(≈88%)
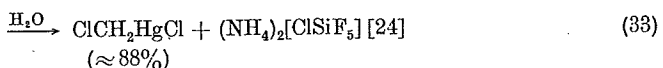
The following compounds were also obtained in this way: C$_6$H$_5$HgCl (69%); CH$_2$=CHHgCl (92%); C$_6$H$_5$HgNO$_3$ (97%); C$_6$H$_5$HgOAc (78%).
Hg(I) salts—even the insoluble Hg$_2$Cl—reacted to form RHgX, but by separation of metallic Hg.

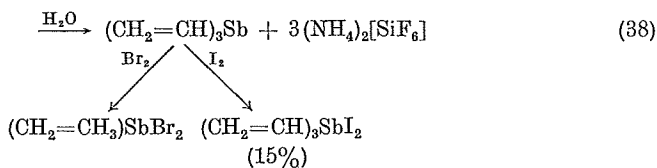Pb: With Pb(OAc)$_4$ one-step-reactions could be performed: [33]

$Pb(OAc)_4 + C_6H_5SiF_3 + HF$

$\xrightarrow{H_2O\ NH_4F} (C_6H_5)_3PbF + (C_6H_5)_2PbF_2 + AcOH + H_2[SiF_6]$ (34)
(75%)   (23%)   (64%)

$Pb(OAc)_4 + 4C_6H_5SiF_3 + 12NH_4F$

$\xrightarrow[highly]{H_2O} (C_6H_5)_4Pb + 4NH_4OAc + 4(NH_4)_2[SiF_6]$ (35)
exothermic   (70%)

the following reactions also occurred:

$2Pb(OAc)_4 + 2(NH_4)_2[RSiF_5] + 8NH_4F$

$\xrightarrow{H_2O} 2RPbF_3 + 2(NH_4)_2[SiF_6] + 8NH_4OAc$ (36)

$R = CH_3{-},\ C_2H_5{-},\ CH_2{=}CH{-}.$

Sb: Because SbF$_3$ is soluble and stable in H$_2$O the following reactions occurred:

$SbF_3 + 3(NH_4)_2[CH_3SiF_5] \xrightarrow[\approx20°C]{H_2O} (CH_3)_3Sb + 3(NH_4)_2[SiF_6]$
spontaneously
-combustible (37)

$SbF_3 + 3(NH_4)_2[CH_2{=}CHSiF_5]$ [33]

$\xrightarrow{H_2O} (CH_2{=}CH)_3Sb + 3(NH_4)_2[SiF_6]$ (38)

$\overset{Br_2}{\swarrow}\quad\overset{I_2}{\searrow}$

$(CH_2{=}CH)_3SbBr_2\quad (CH_2{=}CH)_3SbI_2$
(15%)
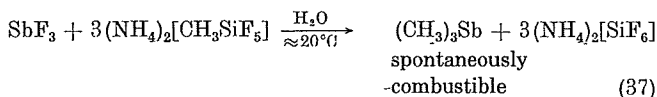
4% $(CH_2{=}CH)_3Sb(I)O(I)Sb(CH{=}CH_2)_3$ was also formed by air oxidation. (see also (51)!) Furthermore the following reactions occurred.

$SbF_3 + 2(NH_4)_2[C_6H_5SiF_5]$

$\xrightarrow{H_2O} (C_6H_5)_2SbF + 2(NH_4)_2[SiF_6]$ (39)
(34%)   (64%)
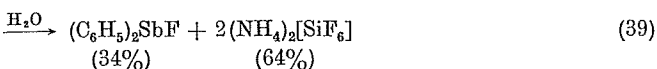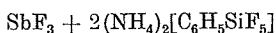
(C$_6$H$_5$)$_2$SbF can likewise be obtained with the water soluble ammoniumpentafluoroantimonate [32]. As to the preparation of (C$_6$H$_5$)$_2$Sb(C$_2$H$_5$) and of (C$_6$H$_5$)$_2$(C$_2$H$_5$)Sb(I)O(I)Sb(C$_2$H$_5$)(C$_6$H$_5$)$_2$ see (51)!

Bi: $Bi(OH)_3 + 3C_6H_5SiF_3 + 6NH_4F + 3HF$

$\xrightarrow{H_2O} (C_6H_5)_3Bi + 3(NH_4)_2[SiF_6] + 3H_2O$ (40)
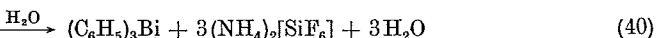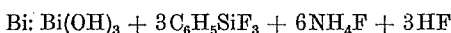
The mixture exothermed violently.

Co: Derivatives of vitamin 12 have been obtained from the "hexafluorosilicate" [34] (see above!)

[Co complex structure] $+ (NH_4)_2[CH_3SiF_5]\cdot NH_4F$

$\xrightarrow{H_2O}$ [Co–CH$_3$ complex structure] $+ (NH_4)_2[SiF_6] + NH_4X$ (41)
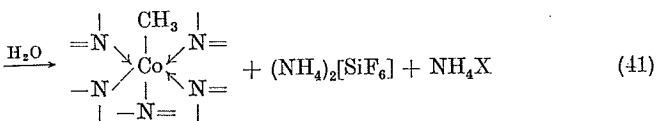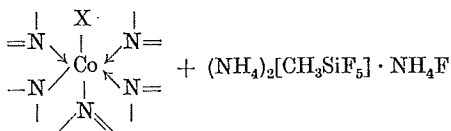
X = CN, HO, Cl, Br, I or a 5'-desoxyadenosyl group

Tl: The following compounds have been prepared in water: [35], [36]

CH$_3$Tl(CN)OAc, [(CH$_3$)$_2$Tl]$^+$[OAc]$^-$, (CH$_3$)$_2$TlCl, RTl(OAc)$_2$,

R=C$_6$H$_5$CH(OCH$_3$)CH$_2$—, n-C$_8$H$_{17}$— und CH$_3$CO$_2$(CH$_2$)$_{10}$—
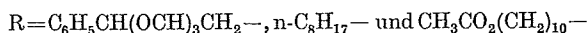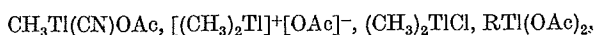
Syntheses of organometallics from silatranes

In the presence of fluoride ions silatranes also give organometallics in H$_2$O and show the color test
For instance the following reaction: [37]

$Bi(OH)_3 + 3 C_6H_5Si(OCH_2CH_2)_3N + 6 NH_4F + 15 HF$

$\xrightarrow{H_2O} (C_6H_5)_3Bi + 3(HOCH_2CH_2)_3N \cdot HF + 3(NH_4)_2[SiF_6] + 3 H_2O$

$$(42)$$
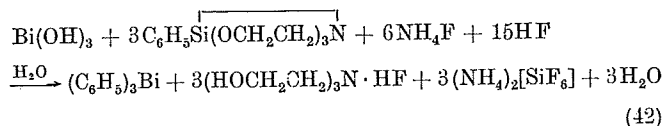
RHgCl (R=CH$_3$— (57%), CH$_2$=CH— (89%), C$_6$H$_5$— (60%), C$_6$H$_5$HgNO$_3$ (60–70%).
R$_3$PbF and R$_2$PbF$_2$ R=CH$_3$ (90%), CH$_2$=CH—(R$_3$PbF = 35%; R$_2$PbF$_2$ = 65%), C$_6$H$_5$—(R$_3$PbF = 10%, R$_2$PbF$_2$ = 85%), (C$_6$H$_5$)$_2$SbF (45%) were also obtained.

Syntheses of hydro- and halocarbons in water [7]

In addition to the already mentioned protonolysis (see (14), (15), (25), (26), (27)!), which have been recently supplemented by the reactions of CuCl and CuF$_2$·2H$_2$O the following observations can be reported:
If acids are added to OPFSs cleavages take place:

$$(NH_4)_2[CH_3SiF_5] + 2 HF \rightarrow CH_3SiF_3 + 2 NH_4HF_2 \qquad (43)$$

If there is an excess of acid or acidic salts even the C—Si bonds are cleaved. The displaced organic groups add hydrogen (protonolysis):

$(NH_4)_2[CH_3SiF_5] + (NH_4)HF_2$

$\xrightarrow{H_2O} CH_4 + [C_2H_6] + (NH_4)_2[SiF_6] + NH_4F \qquad (44)$

$Na_2[CH_2{=}CHSiF_5] + NaHF_2$

$\xrightarrow{H_2O} CH_2{=}CH_2 + Na_2[SiF_6] + NaF \qquad (45)$

$(NH_4)_2[C_6H_5SiF_5] + HF \xrightarrow{H_2O} C_6H_6 + (NH_4)_2[SiF_6] \qquad (46)$
$\phantom{(NH_4)_2[C_6H_5SiF_5] + HF \xrightarrow{H_2O}} (90\%)$

The following one-step reactions are possible:

$CH_2{=}CHCH_2SiF_3 + 2 NH_4F \xrightarrow{H_2O} \{(NH_4)_2[CH_2{=}CHCH_2SiF_5]\}$
$\phantom{CH_2{=}CHCH_2SiF_3 + 2 NH_4F \xrightarrow{H_2O} xxxx} \downarrow NH_4F$
$\phantom{CH_2{=}CHCH_2SiF_3} CH_2{=}CHCH_2 + (NH_4)_2[SiF_6] + NH_3$
$$(47)$$

$CF_2{=}CFSiCl_3 + 5 HF \xrightarrow{H_2O} \{H_2[CF_2{=}CFSiF_5]\} + 3 HCl \qquad (48)$
$\phantom{CF_2{=}CFSiCl_3 + 5 HF \xrightarrow{H_2O} xxxx} \downarrow HF$
$\phantom{CF_2{=}CFSiCl_3 + 5} CF_2{=}CFH + H_2[SiF_6]$
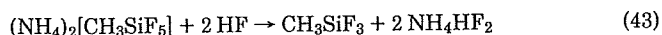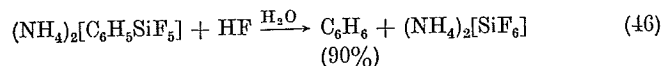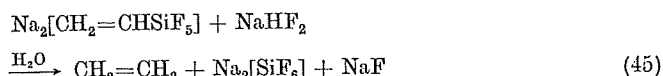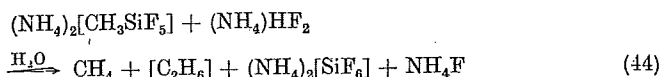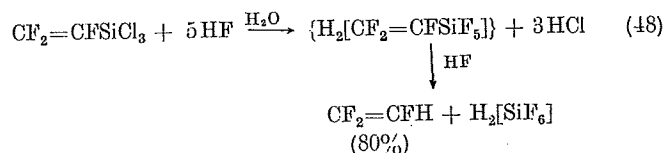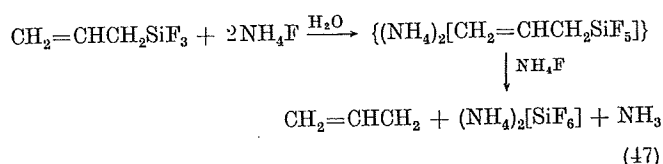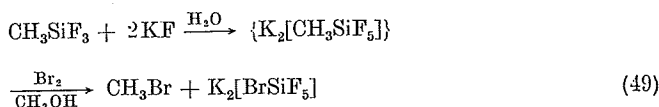$\phantom{CF_2{=}CFSiCl_3 + 5 xx} (80\%)$

The mixture was exothermic.

Halocarbons were obtained with halogens in H$_2$O:

$CH_3SiF_3 + 2 KF \xrightarrow{H_2O} \{K_2[CH_3SiF_5]\}$

$\xrightarrow[CH_3OH]{Br_2} CH_3Br + K_2[BrSiF_5] \qquad (49)$

In some cases we have added an excess of MF for forming the [SiF$_6$]$^{2-}$ because we supposed that it is energetically favoured and that the reactions are facilitated in that way.
Evidently the (NH$_4$)$_2$[CH$_3$SiF$_5$] and K$_2$[CH$_3$SiF$_5$] are completely destroyed by KMnO$_4$ [7]. Only CO$_2$ and MnO$_2$ and a small amount of CH$_4$ were found.

Synthesis with OPFSs in organic fluids

It is astonishing that all the preparations of the forementioned metal organics and organics—for which hitherto chemists considered organic fluids quite unavoidable—run in water. Now we become acquainted with another surprising property of the OPFSs. They easily react in organic fluids although they are in the most cases insoluble therein.
Fascinated by the observation that we could perform so many reactions in water we have still considered reactions in organic fluids as a variation and have demonstrated this behavior only with a few examples:

$(NH_4)_2[CH_3SiF_5] + 3 C_2H_5OH + 3 NH_3$

$\xrightarrow[0°C, exoth.]{C_2H_5OH} CH_3Si(OC_2H_5)_3 + 5 NH_4F \; [7] \qquad (50)$
$\phantom{\xrightarrow[0°C, exoth.]{C_2H_5OH}} (25\%)$

$(C_6H_5)_2SbF + C_2H_5SiF_3 + 2 NH_4F$

$\xrightarrow{AcOH} (C_6H_5)_2Sb(C_2H_5) + (NH_4)_2[SiF_6] \; [33]$
$\phantom{\xrightarrow{AcOH} xxxxxx} \downarrow I_2 + 1/2 O_2$

$(C_6H_5)_2(C_2H_5)Sb(I)O(I)Sb(C_2H_5)(C_6H_5)_2$ (s. auch Gl. (38)!) $\qquad (51)$
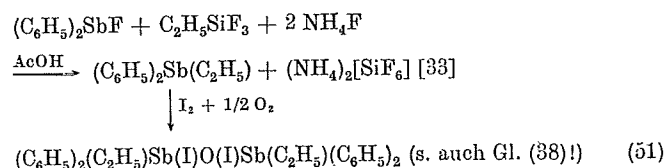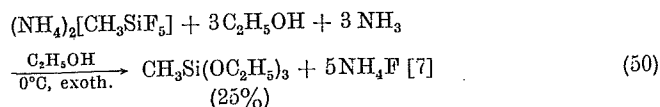
AcOH = glacial acetic acid

$M_2[CH_3SiF_5] + 3 C_2H_5MgBr$

$\xrightarrow{Ether} CH_3Si(C_2H_5)_3 + 3 MgBrF + 2 MF \; [13] \qquad (52)$
$\phantom{\xrightarrow{Ether}} (\approx 25\%)$
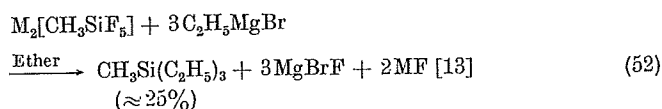
$M = NH_4, K, Na$

Recently this last reaction has been used to prepare 5-norbornen-2-yl-trimethylsilane: [14G], [38]

$$(53)$$
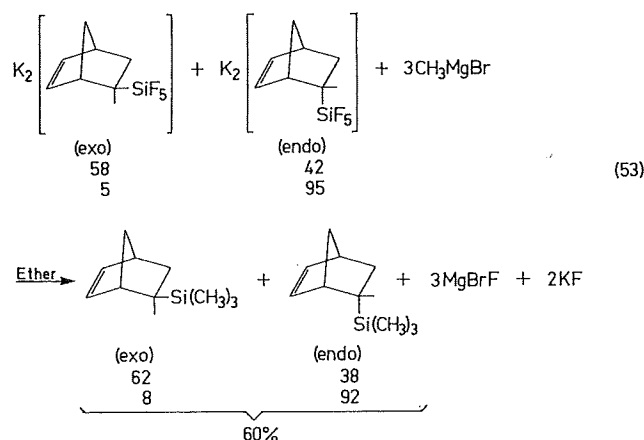
Furthermore we performed:

$Cl_3CSiF_3 + 2 NH_4F \xrightarrow{CH_3CN} \{(NH_4)_2[Cl_3CSiF_5]\}$

$\rightarrow HCCl_3 + NH_3 + (NH_4)_2[SiF_6] \; [24] \qquad (54)$
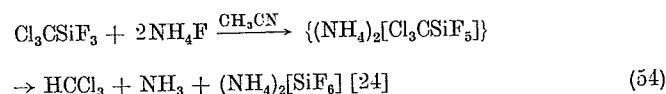
This branch of the OPFS-chemistry by using organic fluids has been developed with eminent success by Kumada and his collaborators.

Syntheses of organometallics with OPFSs in organic fluids

Ag: (E)-alkenyl-PFSs which can be prepared in the following manner give the color test also in organic fluids [39]

$$(55)$$
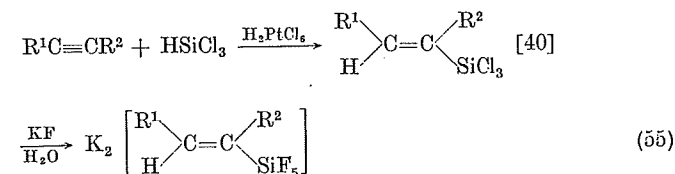
Besides sym. (E,E)-1,3-dienes (R^1 = R^2) of high stereoselectivity and retention of the double bond, biphenyl and biphenylethane were also obtained from Ag salts. (tab. 3)

Terminal and internal alkenyl-PFSs showed no significant differences

Pd: (E)-1-hexenyl-PFS and ethylacrylate gave di-μ-chlorodi-(1-ethoxy-carbonyl-oct-2-enyldipalladium(II) with PdCl$_2$ at 0°C: [14E], [41]

Tab. 3. Color test with Ag salts of the (E)-alkenyl-, phenyl- and aralkyl-PFSs and coupled products formed in organic fluids

R in $K_2[RSiF_5]$	AgF + CH_3CN			AgNO$_3$ + Ether + H$_2$O			comments
	color	yield	R—R[b]	color	yield	R—R[b]	
$C_6H_5CH=CH-$	red purple	74		blue	64		a) isolated yields;
n-$C_4H_9CH=CH-$	blue purple	63	86	red purple	47	66	b) GLC-yields; c) under N$_2$; d) AgBF$_4$;
$CH_3OCH_2CH=CH-$	blue		10	blue	51	61	in CH$_2$Cl$_2$ gave 20–28%
$CH_3O_2C(CH_2)_8CH=CH-$	red	36		blue	65		C$_{16}$H$_{34}$;
$(C_2H_5)_3SiCH=CH-$	red	43	51	blue	58		e) C$_6$H$_6$ > DMF > THF > C$_2$H$_5$OH;
n-C$_4$H$_9$ C$_4$H$_9$-n CH=CH	orange	26		orange	72		f) AgF > AgNO$_3$ > AgBF$_4$
C_6H_5-	orange	82	93	orange	60	69	
$C_6H_5CH_2-$	yellow	46	60[c]	colorless	0		
n-$C_8H_{17}-$[d]	colorless	0[c]		colorless	0		

$2[n\text{-}C_4H_9CH=CHSiF_5]^{2-} + PdCl_2$

$$\xrightarrow[N_2,\ 0°C]{THF} 2\text{-}n\text{-}C_4H_9CH=CHPdCl + [ClSiF_5]^{2-} \qquad (56)$$

$2\,n\text{-}C_4H_9CH=CHPdCl + 2H_2C=CHCO_2C_2H_5 \rightarrow 2\,n\text{-}C_4H_9CH=CHCH_2CO_2C_2H_5$

38%

. With styrene

(19%)

was obtained. Vinyl methyl ketone gave

 (57)

(80%)

Organo-Pd-intermediates are postulated for the following reactions: [14E], [41], [42]

Crosscoupling in the presence of Pd-salts

(E)-$K_2[n\text{-}C_4H_9CH=CHSiF_5]$ + $CH_2=CHCH_2Cl(Br)$

$$\xrightarrow[THF,\ \approx 20°C]{Pd(OAc)_2} (E)\text{-}n\text{-}C_4H_9CH=CHCH_2CH=CH_2 \qquad (58)$$

(71%)

Similarly: $n\text{-}C_4H_9CH=CHCH_2C(CH_3)=CH_2$ (35%), $C_6H_5CH=CHCH_2CH=CH_2$ (40%), $CH_2=CHCH_2CH=CH(CH_2)_6CO_2CH_3$ (55%). This last compound is an intermediate in the synthesis of the naturally occurring recifeiolide [14E], [42].
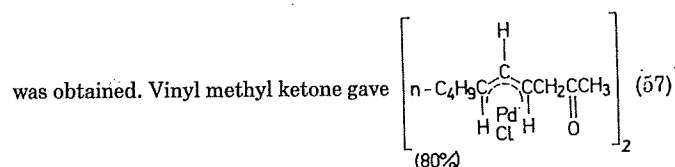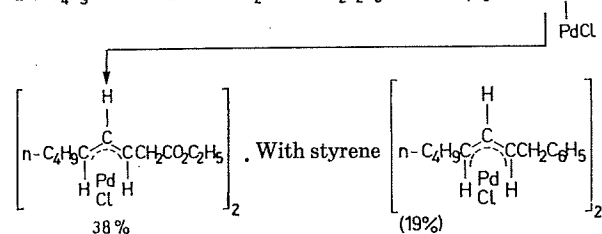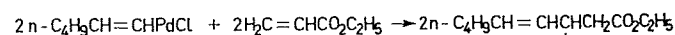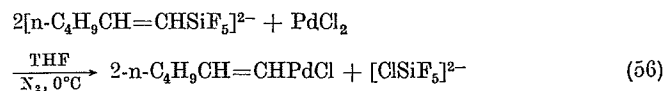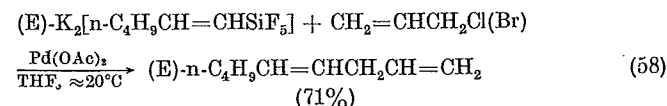In combination with the hydrosilylation in conformity with (54) a regio- and stereoselective transformation of alkynes is possible to (E)-1,4-dienes [14E]. (Exception: 3-chloro-1-butene gave (2,5E)- and (2Z, 5E)-2,5-decadienes).
Activated olefins exchange the H of the double bond for R of the OPFSs

$K_2[n\text{-}C_4H_9CH=CHSiF_5]$ + $CH_2=CHCH$ + $Pd(OAc)_2$
              ‖
              O

$$\xrightarrow[\approx 20°C]{THF} n\text{-}C_4H_9CH=CHCH=CHCH + HPd(OAc) + K_2[AcOSiF_5]$$
                             ‖
                             O

(59)
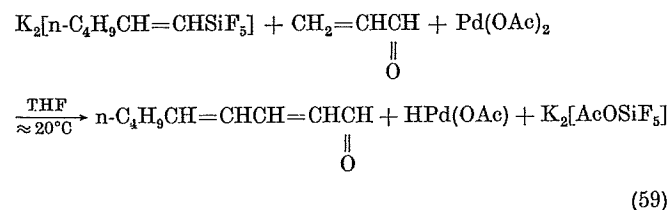
The Pd·salt was reduced and Pd was precipitated in the form of a mirror.
Methyl acrylate or methyl crotonate could be substituted for acrolein.
$CH_2=CHCN$ gave under reflux (E,E)- and (Z,E)-isomers. All reactions of the (E)-alkenyl-PFS were highly stereoselective and only (E,E)-dienes were obtained. The phenyl-PFS also reacted stereoselectively and gave (E)-phenyl-substituted olefins.
Homo couplings as with the reactions of the Ag- or Cu-salts in H$_2$O could be carried out with PdCl$_2$ in organic fluids only with the styrene- and phenyl-PFS [14E], [41] (but cf. 43) too!)

$2K_2[(E)\text{-}C_6H_5CH=CHSiF_5] + PdCl_2$

$$\xrightarrow[20°C,\ 3h]{CH_3CN} (E,\ E)\text{-}C_6H_5CH=CHCH=CHC_6H_5$$
(54%)

$+ K_2[SiF_6] + K_2[Cl_2SiF_4] + Pd \qquad (60)$
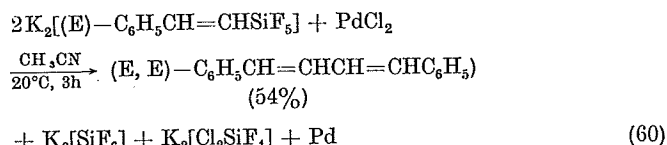
Similarly the phenyl-PFS gave biphenyl (48%) in THF.
At higher temperature the following reaction could be run without organic fluid with PdCl$_2$ (also with other Pd(0) and Pd(II)·complexes): [41]

$K_2[C_6H_5CH=CHSiF_5] + C_6H_5I$

$$\xrightarrow[135°C]{PdCl_2} C_6H_5CH=CHC_6H_5 + (C_6H_5)_2C=CH_2 \qquad (61)$$
        (36%)   (9%)
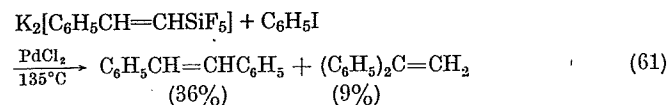
The reaction by exchanging R proceeded in THF in the subsequent manner: [41]

$K_2[C_6H_5SiF_5] + C_6H_5CH=CHBr$

$$\xrightarrow[THF]{Pd(OAc)_2/(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2} (C_6H_5)_2C=CH_2 \qquad (62)$$
(23%)
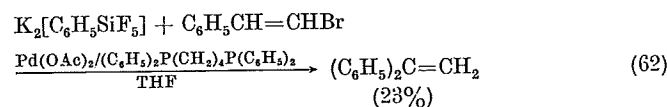
$C_6H_5CH=CHC_6H_5$ was only found in traces.
Carbomethoxylations of the alkenyl-PFS could be performed with CO in CH$_3$OH and stoichiometric amounts of Pd-salts. The NaOAc was evidently necessary to neutralize the HCl [15], [41].

$K_2[CH_3(CH_2)_5CH=CHSiF_5] + CO + PdCl_2$

$$\xrightarrow[\approx 20°C,\ 4h\ 0,1\ MPa]{CH_3OH/NaOAc} CH_3(CH_2)_5CH=CHCO_2CH_3$$
(92%)

$+ HCl + K_2[ClSiF_5] + Pd \qquad (63)$
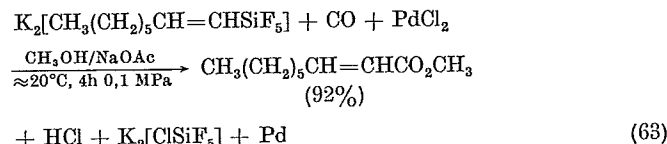
In this way a series of esters RCH=CHCO$_2$CH$_3$ could be produced in which R was (CH$_3$)$_3$C— (90%), C$_6$H$_5$— (76%). Functional groups were tolerated. For instance compounds could be prepared in which R was CH$_3$OCH$_2$— (61%) or CH$_3$O$_2$C(CH$_2$)$_8$— (72%). An ester with an internal double bond was obtained: CH$_3$(CH$_2$)$_3$CH=C(CO$_2$CH$_3$)-(CH$_2$)$_3$CH$_3$ (88%).

56

In combination with the hydrosilylation (see (54)!) the procedure allows the regio- and stereoselective transformation of alkynes to unsaturated (E)-α,β-carboxylic esters.

Cu: *Syntheses with OPFSs in the presence of catalytic or stoichiometric amounts of Cu-salts in organic fluids*
The reaction specified below could be accomplished:

$$K_2\left[\begin{array}{c}R^1\\H\end{array}C=C\begin{array}{c}R^2\\SiF_5\end{array}\right] + R^3OH + O_2$$

$$\xrightarrow[25°C]{Cu(OAc)_2} \left[\begin{array}{c}R^1\\H\end{array}C=C\begin{array}{c}R^2\\OR^3\end{array}\right] \qquad (64)$$
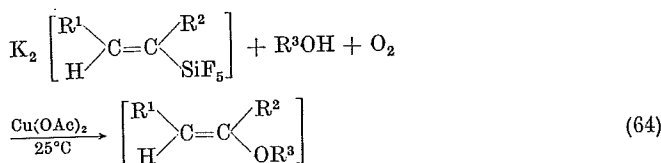
With the suitable alcohols and oxygen the corresponding ethers were prepared:

n-$C_6H_{13}CH=CHOCH_3$ (66%), n-$C_6H_{13}CH=CHOC_2H_5$ (64%),

n-$C_6H_{13}CH=CHOCH_2CH=CH_2$ (62%),

n-$C_6H_{13}CH=CHOCH_2CH=CHCH_3$ (55%),

n-$C_6H_{13}CH=CHOCH_2C=CH_2$ (31%),
$\qquad\qquad\qquad\qquad\qquad |$
$\qquad\qquad\qquad\qquad\quad CH_3$

$C_6H_5CH=CHOCH_3$ (55%), $CH_3O_2C(CH_2)_8CH=CHOCH_3$ (67%),

$NC(CH_2)_2OCH_2CH=CHOCH_3$ (55%).

n-C_4H_9 $C=C$ C_4H_9-n (52%).
$\qquad H \qquad\qquad OCH_3$
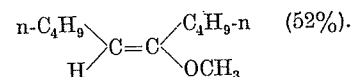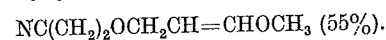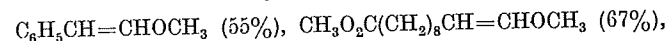
The reactions are highly stereoselective and produce the (E)-alkenylether in an isom. pur. of more than 99%. It is supposed that the mechanism involves a radical ion (see (71)!)
Without alcohols and without oxygen the ester, octenyl acetate, was formed from octenyl-PFS in DMF [45].

$$K_2[(E)\text{-}n\text{-}C_6H_{13}CH=CHSiF_5] + Cu(OAc)_2$$

$$\xrightarrow[20°C]{DMF} (E)\text{-}n\text{-}C_6H_{13}CH=CHOAc + Cu[AcOSiF_5] \qquad (65)$$
$$(31\%)$$

Using H_2O instead of the alcohols and added O_2, aldehydes were prepared [44]:

$$K_2[RCH=CHSiF_5] + H_2O + O_2 \xrightarrow[\approx20°C]{Cu(OAc)_2\atop CH_3CN} RCH_2CHO \qquad (66)$$
$$(50\text{--}52\%)$$

$R = n$-$C_6H_{13}-$, $CH_3O_2C(CH_2)_8CH=CH-$

$$K_2[n\text{-}C_8H_{17}SiF_5] + O_2$$

$$\xrightarrow[20°C,\,50h]{CuCl_2\atop CH_3OH} n\text{-}C_7H_{17}CHO + n\text{-}C_8H_{17}Cl \qquad (67)$$
$$(35\%) \qquad\qquad trace$$

See also (72)!
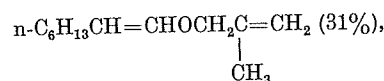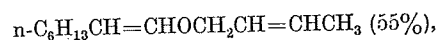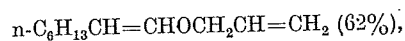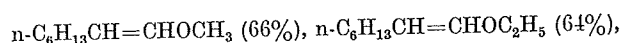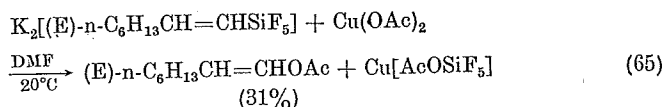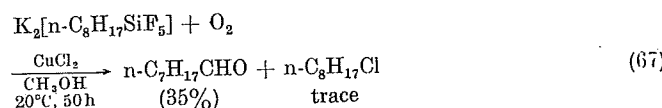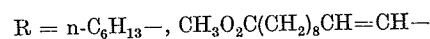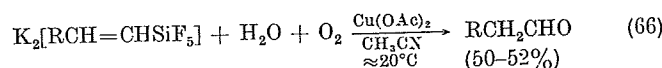
With stoichiometric amounts of $CuCl_2$ and $CuBr_2$ halocarbons were obtained in ether [14F], [45], [46], [47]

$$K_2[RSiF_5] + 2Cu(II)X_2 \xrightarrow[20°C]{Ether} RX + 2Cu(I)X + K_2[XSiF_5] \qquad (68)$$
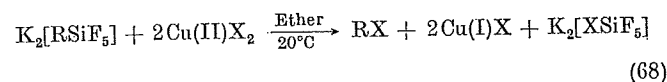
By this procedure n-$C_8H_{17}Br$ (88%), $CH_3CO(CH_2)_4Cl$ (66%), $Br(CH_2)_{11}Cl$ (60%), $CH_2=CHCH_2O(CH_2)_3Br$ (52%) and (E)-1-$CH_2=CH(CH_2)_4Br$ (45%, isom. pur. >99%; no cyclisation product detected) were achieved. The processes ran with retention of the configuration of the alkenyl group and with high stereoselectivity. Furthermore $C_6H_5(CH_3)CHCH_2Br$ (53%), $C_6H_5(CH_3)CH(CH_2)_2Br$ (55%) and $C_6H_5(CH_3)_2CCH_2Br$ (16%) and $C_6H_5(CH_3)_2SiF_3$ (71%) were prepared [49].
The C—Si-linkages of both the exo- and endo-2-norbornyl-PFS were nonstereoselectively cleaved by $CuBr_2$ and mixtures of exo- and endo-2-norbornylbromide were formed [45].

Because the yields of the alkyl products highly decreased in the presence of radical trapping agents

(exception ⬡ —PFS)
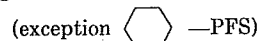
the following radical mechanism is postulated:

$$[RSiF_5]^{2-} + Cu(II)X_2 \to R^\bullet + [XSiF_5]^{2-} + Cu(I)X \qquad (69)$$

$$R^\bullet + Cu(II)X_2 \to RX + Cu(I)X \qquad (70)$$
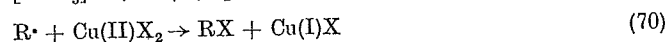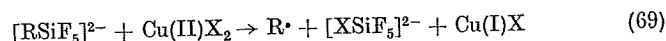
Under the present conditions the copper(I) is probably oxidized to copper(II) by molecular oxygen and can react.
Functional groups are preserved because the processes run at room temperature. $Cu(OAc)_2$ and $Cu(NCS)_2$ were inefficient. Cu-triflate cleaved n-$C_8H_{17}SiF_3$ from $K_2[n\text{-}C_8H_{17}SiF_5]$.
Although the radical trapping agent, nitrosobenzene, also greatly decreased [45] the yield of the reaction of the (E)-1-hexenyl-PFS with $CuBr_2$ (61 → 31%) it is nevertheless guessed that the alkenyl-PFSs do not react through radicals because the configurational stability of the alkenyl group is known to be very low. By proceeding through alkenyl radicals an isomerisation should occur and produce a mixture of (E)- and (Z)-alkenyl halides. But the (E)-1-hexenylbromide had a high stereoselectivity (99%). Therefore a mechanism is postulated through alkenyl-Cu-intermediates and radical ions:

$$[RCH=CHSiF_5]^{\bullet-}/CuX_2^{\bullet-}$$
$$\qquad |$$
$$\quad CuX_2$$
$$\to [RCH=CHCuX_2] + [XSiF_5]^{2-} + CuX \qquad (71)$$
$$\qquad \hookrightarrow RCH=CHX + CuX,$$
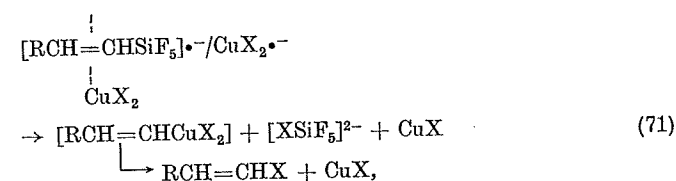
Such Cu-intermediates are known and their decomposition has been studied [48].
However a radical mechanism is proposed for the process of (67): [45]

$$2n\text{-}C_8H_{17}^\bullet + 2O_2 \to 2n\text{-}C_8H_{17}OO^\bullet$$

$$\to n\text{-}C_7H_{15}CHO + n\text{-}C_8H_{17}OH + O_2 \qquad (72)$$
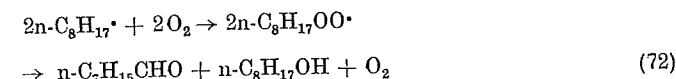
Although the alcohol was not found it could have been oxidized.

Syntheses with m-chloroperoxybenzoic acid (MCPBS) in organic fluids [51]

With peroxyacetic acid in acetic acid, tert-butylhydroperoxide in diglyme or with H_2O_2 the OPFSs gave only $RSiF_3$. But with m-chloroperoxybenzoic acid the corresponding alcohols were obtained in high yields:

$$K_2[CH_3O_2C(CH_2)_{10}SiF_5] + MCBPS$$

$$\xrightarrow[20°C]{DMF} CH_3O_2C(CH_2)_{10}OH + K_2[m\text{-}ClC_6H_4CO_2SiF_5] \qquad (73)$$
$$(77\%)$$

In this manner were prepared:
n-$C_8H_{17}OH$ (82%), n-$C_{12}H_{25}OH$ (75%),

⬡CH_2CH_2OH (54%),

⬡OH (22%), C_6H_5OH (64%), [51]

the highly valuable insect repellent with low irritancy and low toxicity

⬡⬡OH (65%), [14H], [16]

exo-norboranol OH (47%),

$C_6H_5(CH_3)C\overset{H}{\underset{OH}{}}$ (65%), [50]

$C_6H_5(CH_3)CHCH_2OH$ (83%), $C_6H_5(CH_3)CH(CH_2)_2OH$ (92%),
$C_6H_5(CH_3)_2CH_2OH$ (traces) [16].

Syntheses with halogens and N-bromosuccinimide (NBS) in organic fluids

With the halogens (X = Cl, Br, I) halocarbons can be prepared [10], [14B], [47], [52]

$$K_2[RSiF_5] + X_2 \xrightarrow[\substack{0-50\,°C \\ exoth.}]{CCl_4} RX + K_2[XSiF_5] \qquad (74)$$

RX = n-C_8H_{17}Cl (73%), n-C_8H_{17}Br (69%), n-C_8H_{17}I (73%), n-$C_{12}H_{25}$Br (75%), $CH_3O_2C(CH_2)_{10}$Br (85%), C_6H_{11}Cl (54%), C_6H_{11}—Br (67%), C_6H_{11}I (32%), n-C_4H_9CH=CHBr (61%, regio- but only slightly stereoselective, since both (E)- (67%) and (Z)-product) n-C_4H_9CH=CHI (48%, only (E)-product), C_6H_5Br (59%); IBr gave 17% C_6H_{11}—I and 27% C_6H_{11}—Br 90% n-C_4H_9CH=CHI and 3% n-C_4H_9CH=CHBr. With phenyl-PFS only C_6H_5I was formed.

The bromine cleavage of the exo- and endo-2-norbornyl-PFS in CH_3OH or THF proceeded in a highly stereoselective fashion with more than 95% inversion of the configuration at carbon. In C_6H_6 or CCl_4 the endo-compound was nearly completely (98%) transformed to the exo-2-norbornylbromide; but the exo-PFS was only partly converted into the endo-2-norbornylbromide:

$$(75)$$

This result corresponds with the reaction using $CuBr_2$ [45]. N-bromosuccinimid (NBS) can be employed for brominations. Using Rb-, Cs- or K-PFSs the following reactions occurred: [14B], [47], [52]

$$(76)$$

In this way alkylbromides could be prepared: n-$C_{12}H_{25}$Br (75%),

 $(CH_2)_2$Br (54%), Br (79%),

$C_6H_5(CH_2)_2$Br (60%), $CH_3O_2C(CH_2)_{10}$Br (86%), $CH_3CO(CH_2)_4$Br (73%). $K_2[Br(CH_2)_{11}SiF_5]$ was converted into $Br(CH_2)_{11}$Br (73%). Moreover, in combination with hydrosilylation (54) the reactions of NBS allow a regio- and stereoselective transformation of alkynes to alkenylbromides [14B]: (E)-1-hexenyl-PFS yielded 75% hexenylbromide (E/Z = 91/9). The C_6H_5CH=CHBr was only composed of the (E)-compound (83%), for the $CH_3O_2C(CH_2)_8$CH=CHBr (68%) was E/Z = 95/5 and the n-C_4H_9CH=C(Br)C_4H_9-n (70%) E/Z = 99/1. The $CH_3(CH_2)_2$CH=CH$(CH_2)_3$Br gave a yield of 36% (E/Z = 83/17) [14H], [49].

1,2,3,4-Tetrahydronaphthyl bromide, an intermediate in the synthesis of the above mentioned insect repellent, was obtained in a yield of 56% in dioxane. Furthermore

$$CH_3O_2C\text{—}\langle\ \rangle\text{—}Br$$

(36%, m/p = 58/42) was prepared in CH_3OH.

The reactions of 2-norbornyl-PFS with NBS proceed in the same manner as those with Br_2 (75) and $CuBr_2$. Inversion was also observed in this case.

Endo- and exo-norborn-5-en-2-yl-PFS were transformed into the 3-nortricyclyl bromide: [14F], [38]

$$(77)$$

Because the bromination of the "neutral"

with its tetravalent coordinatively unsaturated Si-atom (preparation see (52)!) differs from (77) it could be elucidated in all likelihood, why the Si—C-linkages of the OPFSs can so easily be cleaved. The force-constant of the Si—C-bond of the $[CH_3SiF_5]^{2-}$ has been shown to be much smaller than that of the CH_3SiF_3 [27]. The OPFSs contain double negatively charged, coordinatively saturated Si-atoms which make the bonds highly electron-rich. [14G] In the order $C_6H_5SiF_3$(I) > $C_6H_5Si(CH_3)_3$(II) ≫ $Na_2[C_6H_5SiF_5]$ (III) the ionisation potentials decrease. That of the Si—Cσ bond of III is comparable with those of the phenyl π electrons and with those of the Si—Si-bond which is also easily cleaved. The σ bonding energy levels of I and II lie much lower than those of III. The bond order of the Si—C σ bonds of III is much lower than those of I and II [10].

In the sequence of reactions to prepare the (R)—(−)—α-curcumen the following step has been inserted [53]

$$(78)$$

The product showed low optical purity because of partial racemization [50] $CH_3(C_6H_5)$CHCH$_2$Br, $CH_3(C_6H_5)$CH$(CH_2)_2$Br and $(CH_3)_2(C_6H_5)$-CCH$_2$Br were obtained in the same manner in ether or CH_3OH [49]

Syntheses by pseudohalogens in organic fluids

Alkenyl- (but not alkyl-) PFSs can be transformed to (E)-alkenyl-thiocyanates by copper(II)isothiocyanate [14D], [45], [54]:

$$K_2[RCH=CHSiF_5] + 2 Cu(NCS)_2$$
$$\xrightarrow[\approx 20°C,\, 3h]{DMF} RCH=CHSCN + 2 CuNCS + K_2[(SCN)SiF_5] \qquad (79)$$

KSCN + $CuSO_4 \cdot 5H_2O$ can also be used instead of the pure copper compound. By these procedures (E)-n-C_6H_{13}CH=CHSCN (67–74%), C_6H_5CH=CHSCN (53%), NC$(CH_2)_2$OCH$_2$CH=CHSCN (49%), CH_3O_2C—$(CH_2)_8$CH=CHSCN (70%), n-C_4H_9CH=C(C_4H_9-n)SCN (78%), C_6H_5SCN (42%) and n-C_8H_{17}SCN (trace, difference to the halogenations) were obtained.

Copper(II)selenocyanate $(Cu(OAc)_2 + 2 KSeCN)$ and (E)-1-hexenyl-PFS were allowed to react in DMF. They gave (E,E)-di-1-hexenyl selenide: [14D], [45]

$$2 K_2[(E)\text{-n-}C_4H_9CH=CHSiF_5] + 2 Cu(SeCN)_2$$
$$\xrightarrow[\approx 20°C]{DMF} [(E, E)\text{-n-}C_4H_9CH=CH]_2Se + 2 Cu(SeCN)$$
$$(58\%)$$
$$+ K_2[(SeCN)SiF_5] + K_2[NCSiF_5] \qquad (80)$$

Syntheses with tetracyanoethylene (TCNE) with and without organic fluids [14C], [55]

Because of the four cyano groups the tetracyanoethylene is electron-poor. Therefore it is considered to be a typical one-electron acceptor. It did not react with methyl-PSF. But with ethyl-PSF in CH_3CN suspension a reaction occurred to produce 1,1,2,2-tetracyanobutane

$$K_2[C_2H_5SiF_5] + (NC)_2C=C(CN)_2$$
$$\xrightarrow[\approx 20°C,\, 1h]{CH_3CN} C_2H_5C(CN)_2C(CN)_2^- \qquad (81)$$
$$\xrightarrow{CF_3CO_2H} \begin{array}{c} CN\ \ CN \\ |\ \ \ | \\ C_2H_5C\text{—}CH \\ |\ \ \ | \\ CN\ \ CN \end{array} + K_2[CF_3CO_2SiF_5]$$

In the same way n-$C_8H_{17}(CN)_2C(CN)_2$H (64%) and

$C(CN)_2C(CN)_2$H (34%) were formed.

58

Furthermore the following reactions could be realized:

$$K_2\left[\text{(bicyclic structure)}-SiF_5\right] + TCNE \xrightarrow[CH_3CN]{CF_3CO_2H \atop 3°C, 8h} \text{(bicyclic structure)}-C(CN)_2C(CN)_2H \quad (82)$$

(exo 100%)   (exo/endo = 1:1)

$$\left[\text{(bicyclic structure)}SiF_5\right] + TCNE \xrightarrow{CF_3CO_2H \atop 3°C, 8h} \text{(bicyclic structure)}-C(CN)_2C(CN)_2H \quad (83)$$

(endo 95%)   5%
           (nur exo)

Solid n-octyl-PFS and TCNE (without organic fluid!) by stirring under N_2 vac. and quenching with CF_3CO_2H afforded 80% 1,1,2,2-tetracyanodecane and 13% tricyanodecane:

$$\underbrace{K_2[n\text{-}C_8H_{17}SiF_5] + TCNE}_{\substack{\text{solid} \\ \text{deep violet}}}$$

$$\xrightarrow[\substack{3°C, 8h \\ N_2\text{-Vak.}}]{CF_3CO_2H} n\text{-}C_8H_{17}C(CN)_2C(CN)_2H + n\text{-}C_8H_{17}C(CN)=C(CN)_2$$

(84)

Conclusions see below!

Fluorinations without organic fluids [56]

NaF or $Na_2[SiF_6]$ are not able to fluorinate the Cl—Si-bond; but the following reaction occurred without organic fluid:

$$CH_3SiHCl_2 + Na_2[C_6H_5SiF_5]$$

$$\xrightarrow{0°C} C_6H_5SiF_3 + CH_3SiHF_2 + 2NaCl \quad (85)$$
$$(70\%)$$
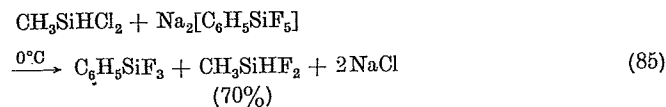
The mixture was exothermic. The HSi-bond was left intact. Also CH_3SiCl_3 with OPFS exothermed and formed CH_3SiF_3 (72–76%). In H_2O $(CH_3)_3SiCl$ and the OPFS became cool $(CH_3)_3SiF$ was formed (71%).

With $C_6H_5CCl_3$, which can be easily fluorinated by other means both $Na[SiF_6]$ and $Na_2[CH_3SiF_5]$ gave $C_6H_5CClF_2$ in the same yield (80–90%). NaF provided $C_6H_5CF_3$ (15%).

Conclusions

The ability of the OPFSs to add $(CN)_2C=C(CN)_2$ increases but the color test is retarded, if their R increases. Therefore it is easily understood that at the very least two other mechanisms must still exist besides a possible radical reaction in agreement with (69).
Especially in H_2O very active anions can be cleaved:

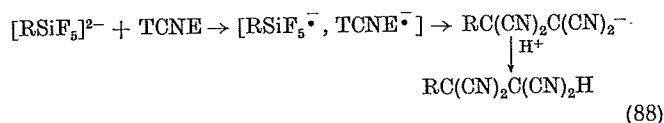$$[RSiF_5]^{2-} + :X^- \rightarrow [XSiF_5]^{2-} + R:^- \quad (86)$$
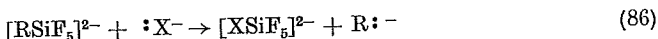
These anions are able to react with a great number of cations or electrophiles and can be transformed by the help of Ag- or Cu-salts into likewise very active radicals:

$$:R^- + Ag^+ \rightarrow AgR \rightarrow Ag\cdot + R\cdot \quad (87)$$
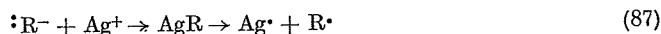
Finally R· can homo-couple (R—R) mostly at room temperature. In organic fluids (see (71) particularly in the reactions in the solid state the OPFSs are good electron-donors and an initial one-electron transfer will play an important part.
Electron spin resonance studies have proved that the formation of radical anions dominates the reactions: [14C], [55], [56]

$$[RSiF_5]^{2-} + TCNE \rightarrow [RSiF_5^{\cdot-}, TCNE^{\cdot-}] \rightarrow RC(CN)_2C(CN)_2^{-}$$
$$\downarrow H^+$$
$$RC(CN)_2C(CN)_2H$$

(88)

The successful reaction in the solid state (see (84)!) demonstrates that this one-electron transfer can occur even at the solid surface of the OPFSs. This perhaps also causes the OPFSs to react in organic fluids although they are not soluble.
The great number of the above mentioned reactions show that the OPFSs are a new class of compound which is universally suited for metalorganic and organic syntheses even at room temperature.

Prospects

The reaction (84) with its mild conditions perhaps allows a profound insight into solid state chemistry. Although differences are found between the aptitude of the organic fluids the transactions in them are perhaps also solid state reactions.
It ought to be accurately elaborated that the OPFSs are color reagents for the qualitative determination of silver. If AgOAc does not give the color test [39] it is only necessary to add a drop of HNO_3.
Alternatively the Ag-salts are reagents for the qualitative indication of the OPFSs, which can be used in thin layer chromatography [8] e.g. for the analysis of a silicone resin. With Ag- or Cu-salts and "bivalent" OPFSs, e.g. $M_4[F_5SiCH=CHCH=CHSiF_5]$ or $M_4[F_5SiCCl=CClSiF_5]$ (starting compounds see [58]–[61]) cyclic hydrocarbons or linear oligomers and even polymers can probably be obtained with groups —CH=CHCH=CH— etc. "Monovalent" $M_2[RSiF_5]$ could terminate the chains. From $HC(SiCl_3)_3$ [62] or $C(SiCl_3)_4$ [58], [60], [61] (perhaps only briefly stable) "tri- and tetravalent" OFPSs can be used for branching.
Because Clark and Willis [63] have prepared $K_2[CF_3GeF_5]$ it is perhaps possible to perform several reactions of the OPFSs with organofluorogermanates.

[1] Booth, H. S., Carnell, P. H., J. Am. Chem. Soc. 68 (1946) 2650
[2] Booth, H. S., Martin, W. F., ibid 68 (1946) 2655
[3] Tansjö, L., Acta chem. Scand. 15 (1961) 1583
[4] Tansjö, L., ibid 18 (1964) 456
[5] Tansjö, L., ibid 18 (1964) 465
[6] Müller, R., Dathe, C., J. prakt. Chem. [4] 22 (1963) 232
[7] Müller, R., Dathe, C., Z. anorg. allg. Chemie 341 (1965) 41
[8] Müller, R., Dathe, C., ibid 341 (1965) 49
[9] Müller, R., Organomet. Chem. Rev. 1 (1966) 359
[10] Tamao, K., Yoshida, J., Yamamoto, H., Kakui, T., Matsumoto, H., Takahashi, M., Kurita, A., Murata, M., Kumada, M. Organometallics 1 (1982) 355
[11] Müller, R. in Gutmann, V., Proc. Int. Conf. on Coordin. Chem., Wien, New York (1964) 173
[12] Müller, R., Dathe, C., Chem. Ber. 98 (1965) 235
[13] Müller, R., Z. Chem. 5 (1965) 220
[14] Yoshida, J., Organic Synthesis via Organopentafluorosilicates (1981) Kyoto Univ. A.) S. 7 ff; B.) S. 22 ff; C.) S. 44 ff; D.) S. 54 ff; E.) S. 71 ff; F.) S. 87 ff; G.) S. 98 ff; H.) S. 109 ff
[15] Tamao, K., Kakui, T., Kumada, M., Tetrah. Lett. No 7 (1979) 619
[16] Tamao, K., Yoshida, J., Akita, M., Sugihara, Y., Iwahara, T., Kumada, M., Bull. Chem. Soc. Jpn. 55 (1982) 255
[17] Müller, R., D. P. (DDR) 5896 (1943/53); Chem. Zbl. (1950/54) 64315
[18] Moscony, J. J., Mc Diarmid, A. G., Chem. Commun No 14 (1965)
[19] Müller, R., Köhne, R., Model, H.-J., Dathe, C., Z. anorg. allg. Chemie 368 (1969) 243
[20] Müller, R., Dathe, C., ibid 343 (1966) 150
[21] Klanberg, F., Muetterties, E. L., Inorg. Chem. 7 (1968) 155
[22] Kumada, M., Tamao, K., Hayashi, T., Akita, M., 14th Central Regional Meeting, Midland, Mich. (1982) 89
[23] Müller, R., Dathe, C., Mroβ, D., Chem. Ber. 98 (1965) 241
[24] Müller, R., Reichel, S., ibid 98 (1965) 3874
[25] Müller, R., Dreβler, M., Dathe, C., J. prakt. Chem. [4] 312 (1970) 150
[26] Kuroda, K., Jshikawa, N., Nippon Kagaku, Zasshi 91 (1970) 77
[27] Licht, K., Peuker, C., Dathe, C., Z. anorg. allg. Chem. 380 (1971) 293

[28] Marat, R. K., Janzen, A. F., Can. J. Chem. *55* (1977) 1167

[29] Marat, R. K., Janzen, A. F., J. Chem. Soc. Comm. (1977) 671

[30] Krause, E., Schmitz, M., Chem. Ber. *52* (1919) 2159

[31] Yoshida, J., Tamao, K., Kakui, T., Kumada, M., Tetrah. Lett. No 13 (1979) 1141

[32] Müller, R., Dathe, C., Chem. Ber. *99* (1966) 1609

[33] Müller, R., Reichel, S., Dathe, C., Inorg. Nucl. Chem. Lett *3* (1967) 125

[34] Penasse, L., Barthelemy, P., BRD Offenl. 2 149 740 (1971/72)

[35] Kurosawa, H., Fukumoto, T., Okawa, R., Inorg. Nucl. Chem. Lett *5* (1969) 473

[36] Kurosawa, H., Yasuda, M., J. chem. Soc., Chem. Commun (1978) 716

[37] Müller, R., Dathe, C., Frey, H.-J., Z. anorg. allg. Chem. *368* (1969) 113

[38] Tamao, K., Mishima, M., Yoshida, J., Takahashi, M., Ishida, N., Kumada, M., J. organomet. Chem. *225* (1982) 151

[39] Tamao, K., Matsumoto, H., Kakui, T., Kumada, M., Tetrah. Lett. No 13 (1979) 1137

[40] Speier, J., Webster, J., Barnes, G., J. Am. Chem. Soc. *79* (1957) 974

[41] Yoshida, J., Tamao, K., Yamamoto, H., Kakui, T., Uchida, T., Kumada, M., Organometallics *1* (1982) 542

[42] Yoshida, J., Tamao, K., Takahashi, M., Kumada, M., Tetrah. Lett. No 25 (1978) 2161

[43] Weber, W. P., Felix, R. A., Willard, A. K., König, K. E., Tetrah. Lett. (1971) 4701

[44] Tamao, K., Kakui, T., Kumada, M., Tetrah. Lett. Vol. 21 (1980) 4105

[45] Yoshida, J., Tamao, K., Kakui, T., Kurita, A., Murata, M., Jamada, K., Kumada, M., Organometallics *1* (1982) 369

[46] Yoshida, J., Tamao, K., Kurita, A., Kumada, M., Tetrah. Lett. No 21 (1978) 1809

[47] Tamao, K., Yoshida, J., Murata, M., Kumada, M., J. Am. Chem. Soc. *102* (1980) 3267

[48] Whitesides, G. M., Casey, C. P., Krieger, J. K., ibid *93* (1971) 1379

[49] Tamao, K., Yoshida, J., Akita, M., Sugihara, Y., Iwahara, T., Kumada, M., Bull. Chem. Soc. Japan *55* (1982) 255

[50] Hayashi, T., Tamao, K., Katsuro, Y., Nakae, I., Kumada, M., Tetrah. Lett. *21* (1980) 1871

[51] Tamao, K., Kakui, T., Kumada, M., J. Am. Chem. Soc. *100* (1978) 2268

[52] Tamao, K., Yoshida, J., Takahashi, M., Yamamoto, H., Kakui, T., Matsumoto, H., Kurita, A., Kumada, M., ibid *100* (1978) 290

[53] Tamao, K., Hayashi, T., Matsumoto, H., Yamamoto, H., Kumada, M., Tetrah. Lett. No 23 (1979) 2155

[54] Tamao, K., Kakui, T., Kumada, M., ibid Nr. 21 (1980) 111

[55] Yoshida, J., Tamao, K., Kumada, M., J. Am. Chem. Soc. *102* (1980) 3269

[56] Tamao, K., Yoshida, J., Kumada, M., Yuki Gosei Kagaku Kyo-kaishi Japan *38* (1980) 769

[57] Müller, R., Dathe, C., Frey, H-J., Chem. Ber. *99* (1966) 1614

[58] Müller, R., Beyer, H., Chem. Ber. *92* (1959) 1018

[59] Müller, R., Beyer, H., ibid *92* (1959) 1957

[60] Müller, R., Müller, W., ibid *96* (1963) 2894

[61] Müller, R., Müller, W., ibid *97* (1964) 1111

[62] Müller, R., Seitz, G., ibid *91* (1958) 22

[63] Clark, H. C., Willis, C. J., J. Am. Chem. Soc. *84* (1962) 898

Address of the author:
GDR 8122 Radebeul
Hoflössnitzstrasse
4a/527/10