

Fluorination of $C_6F_5MX_3$ compounds ($M=Si, Ge; X=F, Cl, Br, Alk$) with xenon difluoride and $XeF^+ Y^-$ salts*

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Abstract

Compounds of the formula $C_6F_5MX_3$ ($M=Si, Ge; X=Cl, Br$) react with XeF_2 , exchanging chlorine (bromine) atoms for fluorine. Interaction of $C_6F_5MX_3$ ($X=F, Alk$) with XeF_2 in the presence of $BF_3 \cdot OEt_2$ or with $XeF^+ NbF_6^-$ proceeds by the addition of two fluorine atoms to the pentafluorophenyl ring.

Introduction

Polyfluoroaromatic compounds containing Cl, Br, H, Oalk, NO_2 or CF_3 as substituents in addition to fluorine react with xenon difluoride in the presence of fluoride ion acceptors (acidic conditions) to form 1,4-cyclohexadiene or dihydronaphthalene derivatives [1]. The effect of XeF_2 on polyfluoroaromatics containing a heteroatom in a side-chain has, however, been virtually ignored. Bardin *et al.* [2] have shown that pentafluorophenyl-containing silanes $(C_6F_5)_nSiMe_{4-n}$ ($n=1, 2, 4$) react with XeF_2 and CsF in MeCN (basic conditions) (20–40 °C) to give pentafluorobenzene and decafluorobiphenyl. The reaction of XeF_2 with $B(C_6F_5)_3$ in CH_2Cl_2 below –40 °C (acidic conditions) allows the isolation of $C_6F_5Xe^+$ salts in high yield [3–5]. In MeCN (basic conditions), XeF_2 reacts with $B(C_6F_5)_3$ at higher temperatures to yield the $[MeCN \cdot XeC_6F_5]^+$ cation in addition to several by-products [6]. Following the discovery of the pentafluorophenylxenon cation, extensive research of the properties and reactivity of this unusual electrophile has commenced [7–9]. This has made an investigation of the reactions of XeF_2 with polyfluorinated aryl organoelement compounds necessary, a situation where xenon difluoride could behave as an oxidant as well as an electrophile.

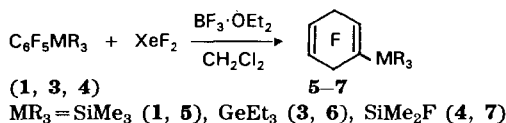
It should be noted in this connection that the reactivity of xenon difluoride is very similar to that of halogen fluorides. In particular, in the presence of Lewis acids, ClF_3 , BrF_3 , BrF_5 [10] and IF_5 [11] fluorinate polyfluoroaromatic

*Dedicated to Prof. Dr P. Sartori on the occasion of his 60th birthday.

compounds in just the same way as XeF_2 . However, pentafluorophenyl-containing silanes $(\text{C}_6\text{F}_5)_n\text{SiMe}_{4-n}$ or $\text{C}_6\text{F}_5\text{SiF}_3$ react with BrF_3 , BrF_5 and IF_5 preferentially in basic medium to form the organic derivatives of polyvalent halogens $\text{C}_6\text{F}_5\text{BrF}_n$ ($n=2, 4$) and $\text{C}_6\text{F}_5\text{IF}_4$ [12–17] in good yield. The inertness of XeF_2 towards $(\text{C}_6\text{F}_5)_n\text{SiMe}_{4-n}$ ($n=1, 2$) under these conditions [2] led us to increase the reactivity of XeF_2 by introducing fluoride ion acceptors, and to investigate the interaction of XeF_2 , $\text{XeF}_2\text{-BF}_3\cdot\text{OEt}_2$ and $\text{XeF}^+ \text{Y}^-$ with $\text{C}_6\text{F}_5\text{SiX}_3$ and $\text{C}_6\text{F}_5\text{GeX}_3$ ($\text{X}=\text{halogen}$).

Results and discussion

Trimethylsilylpentafluorobenzene (1), dimethylbis(pentafluorophenyl)silane (2) and triethylgermylpentafluorobenzene (3) do not react with XeF_2 in CH_2Cl_2 at 20–40 °C. In the presence of $\text{BF}_3\cdot\text{OEt}_2$ as a fluoride ion acceptor, the reactivity of XeF_2 increases dramatically due to xenon–fluorine bond polarization, so that at room temperature compounds 1, 3 and 4 are quickly converted to the 1-substituted heptafluoro-1,4-cyclohexadienes (5–7).



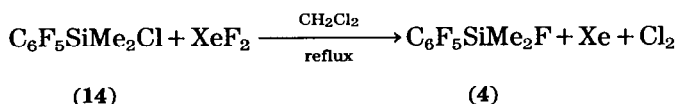
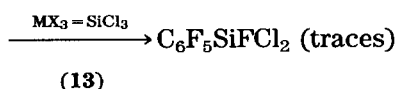
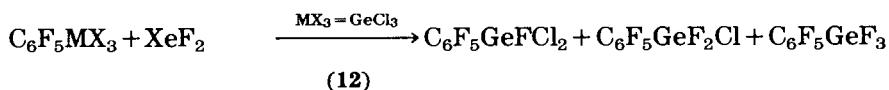
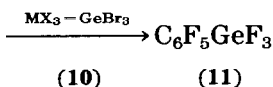
The reaction of excess XeF_2 with $(\text{C}_6\text{F}_5)_2\text{SiMe}_2$ and $\text{BF}_3\cdot\text{OEt}_2$ leads mainly to bis(heptafluoro-1,4-cyclohexadien-1-yl)dimethyl-silane (8), but the product of the fluorination of one pentafluorophenyl ring (9) has also been isolated.



As shown by GLC and ^{19}F NMR data, the fluorination of compounds 1, 2 and 4 by xenon difluoride and $\text{BF}_3\cdot\text{OEt}_2$ in CH_2Cl_2 leads to the formation of traces of hexafluorobenzene (not more than 1 or 2%).

For compounds containing silicon- and germanium-bonded alkyl groups substituted by chlorine and bromine, one could expect not only aromatic ring fluorination but also halogen exchange for fluorine. Indeed, tribromogermypentafluorobenzene (10) readily reacts with XeF_2 at 25–30 °C in CH_2Cl_2 in the absence of a catalyst to form trifluorogermypentafluorobenzene (11), xenon and bromine. But with trichlorogermypentafluorobenzene (12), chlorine exchange for fluorine is much slower. Along with the starting germane 12 and the final germane 11, the reaction mixture contains a considerable amount of intermediate products $\text{C}_6\text{F}_5\text{GeFCl}_2$ and $\text{C}_6\text{F}_5\text{GeF}_2\text{Cl}$. Heating compound 12 and XeF_2 at 66 °C gives a 1:2.75 mixture of $\text{C}_6\text{F}_5\text{GeF}_2\text{Cl}$ and $\text{C}_6\text{F}_5\text{GeF}_3$, and at temperatures above 100 °C, $\text{C}_6\text{F}_5\text{GeF}_3$ and the products of fluorination of the aromatic ring are formed. Trichlorosilylpentafluorobenzene (13) is less reactive than trichlorogermypentafluorobenzene. Re-

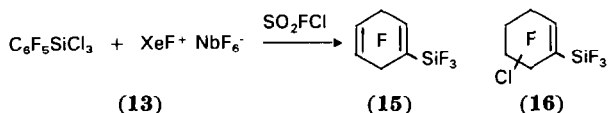
fluxing the mixture with XeF_2 in CH_2Cl_2 leads to formation of only traces of $\text{C}_6\text{F}_5\text{SiFCl}_2$. But chlorodimethylsilylpentafluorobenzene (14) is readily transformed into fluorodimethylsilylpentafluorobenzene (4).



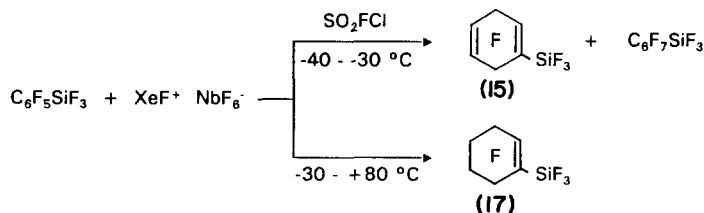
Addition of $\text{BF}_3 \cdot \text{OEt}_2$ to a mixture of $\text{C}_6\text{F}_5\text{GeCl}_3$ or $\text{C}_6\text{F}_5\text{SiCl}_3$ with XeF_2 in CH_2Cl_2 (40 °C) does not essentially change the product composition. No oxidation of the aromatic ring takes place, either. It should be mentioned that trifluorosilyl- and trifluorogermyl-pentafluorobenzenes also do not react with $\text{XeF}_2 - \text{BF}_3 \cdot \text{OEt}_2$ at 40 °C in CH_2Cl_2 .

To increase the reactivity of xenon difluoride, we used niobium pentafluoride as a stronger Lewis acid. NbF_5 reacts with xenon difluoride giving the salts $\text{XeF}^+ \text{NbF}_6^-$ or $\text{Xe}_2\text{F}_3^+ \text{NbF}_6^-$ [18]. Since CH_2Cl_2 reacts vigorously with $\text{XeF}^+ \text{NbF}_6^-$, we used SO_2FCl as the solvent. It should be noted that niobium pentafluoride is virtually unreactive with $\text{C}_6\text{F}_5\text{SiCl}_3$ in SO_2FCl (20–30 °C, 20 min), whereas on heating above 120–130 °C in the absence of a solvent $\text{C}_6\text{F}_5\text{SiCl}_3$ reacts with NbF_5 and $\text{C}_6\text{F}_5\text{SiF}_3$ is distilled off in good yield. Trichlorogermylpentafluorobenzene distills unchanged from the NbF_5 solution.

Addition of XeF_2 to the SO_2FCl solution of $\text{C}_6\text{F}_5\text{SiCl}_3$ and NbF_5 at –30 to –40 °C brings about immediate liberation of a gas. After the addition of more than a half of the reagent, the liberation of gas ceases. Heating the solution to –10 °C again leads to gas liberation. The mixture was heated to 8–10 °C and the volatile products were collected. Their subsequent distillation gave a colourless liquid whose main components were 1-trifluorosilylheptafluoro-1,4-cyclohexadiene (15) and, possibly, an isomeric mixture of 1-trifluorosilylchlorooctafluorocyclohexene (16) (15:16 = 1:2) (^{19}F NMR data). The product 16 could not be isolated by distillation, but its presence was indicated by the signals of three AB systems [$J_{\text{AB}} = \sim 250\text{--}290$ Hz] in the 27–72 ppm range and an SiF_3 group signal of corresponding intensity at 29 ppm. One can suggest that compound 16 is obtained as a result of the chlorofluorination of a heptafluoro-1,4-cyclohexadien-1-yl fragment of an organylsilane by the electrophilic chlorinating intermediate formed as a result of the transformation of $-\text{SiCl}_3$ to $-\text{SiF}_3$ by $\text{XeF}^+ \text{NbF}_6^-$.



Interaction of $\text{C}_6\text{F}_5\text{SiF}_3$ with $\text{XeF}^+ \text{NbF}_6^-$ in SO_2FCl occurs at -40°C to -30°C with gas liberation. The main reaction product is cyclohexadiene (15). In addition to the signals of this compound, the ^{19}F NMR spectrum of the reaction product contained the signals of other unsaturated compounds which are possibly isomers of the diene 15. The elemental analysis data for the set of fluorination products corresponded to the formula $\text{C}_6\text{F}_{10}\text{Si}$.



Treatment of this mixture with niobium pentafluoride in SO_2FCl (20°C) led to a decreased intensity of the signals of diene 15 and an increased intensity for the signals at 69.4, 51.5, 36.9, 16.4 and 12.6 ppm (1:2:2:1:1) which may be assigned to the fluorine atoms of 1-trifluorosilyl-heptafluoro-1,3-cyclohexadiene.* It is important that the elemental composition (C, F) does not change during this process. Treatment of $\text{C}_6\text{F}_5\text{SiF}_3$ with excess $\text{XeF}^+ \text{NbF}_6^-$ from -30°C to 80°C led to trifluorosilylnonafluorocyclohexene (17).

The reaction of $\text{C}_6\text{F}_5\text{GeF}_3$ with $\text{XeF}^+ \text{NbF}_6^-$ at -40°C to -30°C proceeds in a similar manner. The products are 1-trifluorogermyl-heptafluoro-1,4-cyclohexadiene (18) and polyfluorinated unsaturated compounds. The ^{19}F NMR signals of the latter have the same fine structure as those of the respective products of the fluorination of $\text{C}_6\text{F}_5\text{SiF}_3$ but differ in chemical shift values. Treatment of $\text{C}_6\text{F}_5\text{GeF}_3$ with xenon difluoride at $20\text{--}40^\circ\text{C}$ in the presence of SbF_3 (catalyst) gives a mixture of cyclohexadiene (18) and 1-trifluorogermyl-nonafluorocyclohexene (19) (2:1). Further fluorination of this mixture by xenon difluoride leads to olefin 19.

The new compounds 4–9, 17 and 19 have been characterized by elemental analysis, IR, ^1H and ^{19}F NMR data. The chemical shifts and coupling constants of the fluorine signals in the ^{19}F NMR spectra of compounds 5–18 unambiguously indicate the structures of 1-substituted-heptafluoro-1,4-cyclohexadienes [19–23]. The IR spectra of compounds 5–9 exhibit vibration bands at $1772\text{--}1774\text{ cm}^{-1}$ ($\text{FC}=\text{CF}$) and at $1680\text{--}1684\text{ cm}^{-1}$ ($\text{FC}=\text{CMX}$). The ^{19}F NMR spectra of compounds 17 and 19 are typical for 1-substituted-nonafluorocyclohexenes [19].

*Reliable structural identification of substituted heptafluoro-1,3-cyclohexadienes by their ^{19}F NMR spectra in a mixture is impossible because of the unavailability of spectrum–structure correlations for these compounds in the literature.

Experimental

^1H and ^{19}F NMR spectra were recorded on Bruker WP 200 SY and AC 200 instruments (^1H at 200 MHz frequency, internal standard TMS; ^{19}F at 188.3 MHz frequency, internal standard C_6F_6 , $\delta(\text{CFCl}_3) = +162.9$ ppm). IR spectra were recorded on a Specord M 80 instrument using a thin layer. GLC analysis was carried out on an LKhM 72 instrument (15% SKTFT 803 on Chromosorb W). Dichloromethane was dried with P_4O_{10} and distilled. SO_2FCl was distilled twice over SbF_5 . Niobium pentafluoride was distilled in an apparatus constructed of quartz and Kel-F. $\text{XeF}^+ \text{NbF}_6^-$ was prepared according to literature methods [18]. All experiments were performed in a dry argon atmosphere. Tables 1–3 give the NMR, IR and analytical data of the new compounds.

Fluorination of $\text{C}_6\text{F}_5\text{SiMe}_3$ (1)

Compound **1** (13.9 g, 58 mmol), 15 ml CH_2Cl_2 and a few drops of $\text{BF}_3 \cdot \text{OEt}_2$ were placed in a quartz flask. Then XeF_2 (11.0 g, 64.7 mmol) was added in portions with stirring and cooling (cold water). The mixture was stirred for 30 min, 10 ml water added, the organic layer separated, the mixture dried with CaCl_2 and the solvent distilled off. According to ^{19}F NMR data, the reaction mixture contained traces of hexafluorobenzene and 1-trimethylsilylheptafluoro-1,4-cyclohexadiene (**5**) (nc). The latter was isolated by distillation. Yield 11.9 g (74%).

Fluorination of $(\text{C}_6\text{F}_5)_2\text{SiMe}_2$ (2)

Compound **2** (5.7 g, 14.5 mmol) was reacted with 6.6 g (38.8 mmol) of XeF_2 , 15 ml CH_2Cl_2 and a few drops of $\text{BF}_3 \cdot \text{OEt}_2$. After reaction, the mixture (5.5 g) contained traces of C_6F_6 , 1-dimethylpentafluorophenylsilylheptafluoro-1,4-cyclohexadiene (**9**) (nc) and bis(heptafluoro-1,4-cyclohexadien-1-yl)dimethylsilane (**8**) (nc) (NMR data) yields (11% and 55%, respectively, by GLC). Compounds **8** and **9** were isolated by preparative GLC methods.

Fluorination of $\text{C}_6\text{F}_5\text{GeEt}_3$ (3)

Compound **3** (13.1 g, 40.1 mmol), XeF_2 (9.1 g, 53.5 mmol), 15 ml CH_2Cl_2 and a few drops of $\text{BF}_3 \cdot \text{OEt}_2$ were reacted to give, after removal of solvent, a mixture containing C_6F_6 (traces) and 1-triethylgermylheptafluoro-1,4-cyclohexadiene (**6**) (nc) (NMR data). Distillation afforded 10.6 g (72%) of compound **6**.

Fluorination of $\text{C}_6\text{F}_5\text{SiMe}_2\text{F}$ (4)

Compound **4** (3.40 g, 13.9 mmol), 6 ml CH_2Cl_2 , 2.50 g (14.7 mmol) of XeF_2 and a few drops of $\text{BF}_3 \cdot \text{OEt}_2$ were refluxed for 1 h and then distilled to yield 0.2 g of the starting silane **4** and 2.4 g (61%) of 1-fluorodimethylsilylheptafluoro-1,4-cyclohexadiene (**7**) (nc).

TABLE 1
 NMR spectral data

Compounds (nc)	¹ H NMR δ (ppm)	¹⁹ F NMR δ (ppm)						J (Hz)
		F-M	F-2	F-3	F-4	F-5	F-6	
4	0.60 (SiMe ₂ F)	5.31	34.6	1.25	12.5	1.25	34.6	(2, 4)=(4, 6), 4; (3, 4)=(4, 5), 20; (2, 3)=(5, 6), n.d. ^c ; (F-Si-CH ₃), 12.5.
5	0.34 (SiMe ₃)		47.8	49.4	2.75	11.1	66.0	(2, 3), 23.5; (2, 4), 2; (2, 6), 10; (3, 4), 18; (3, 5)=(4, 6), 11; (3, 6), 5; (4, 5), 5; (5, 6), 22.
6	1.14-1.09 (GeEt ₃)		47.6	49.8	2.90	11.6	67.2	(2, 3), 25; (2, 4), 2; (2, 5) 1; (2, 6), 10; (3, 4), 19; (3, 5)=(4, 6), 11; (3, 6), 5; (4, 5), 5; (5, 6), 23.
7 ^a	0.57 (SiMe ₂ F)	2.76	49.6	49.2	2.43	10.4	62.9	(2, 4), 1.5; (2, 6), 10; (3, 4), 19; (3, 5)=(4, 6), 11; (3, 6), 4.5; (5, 6), 22; (F-Si-CH ₃), 7.5.
8 ^a	0.70 (SiMe ₂)		52.9	49.2	3.91	11.5	66.5	(2, 3), 25; (2, 4), 2; (3, 4), 19; (3, 5)=(4, 6), 11; (3, 6)=(4, 5), 5; (5, 6), 21.
9 ^a	0.74 (SiMe ₂)	35.3 (o) 1.70 (m) 13.1 (p)	51.2	49.3	3.67	11.4	66.3	(2, 3), 23.5; (2, 6), 10; (3, 4), 19; (3, 5)=(4, 6), 11; (3, 6)=(4, 5), 5; (5, 6), 22; C ₆ F ₅ group, n.d. ^b
15 ^a		26.9	59.5	48.3	4.36	11.2	65.9	(2, 3), 22.5; (2, 4), 2; (2, 5), 1.5; (2, 6), 10.5; (3, 4), 20; (3, 5), 11; (3, 6), 4.5; (4, 5), 4.5; (4, 6), 10; (5, 6), 21.
17		28.4	64.7	41.6	27.7	27.7	60.5	
18 ^a		11.5	63.8	50.3	7.14	13.3	68.9	(2, 3), 22; (2, 4)=(2, 5), 1.5; (2, 6)=(4, 6), 10; (3, 4), 20; (3, 5), 11; (3, 6), 4; (4, 5), 3.5; (5, 6), 21.
19		14.2	71.1	45.2	31.3	31.9	65.4	

^aAt 45 °C.^bNo first order analysis possible.^cn.d.=not determined.

Fluorination of C₆F₅SiMe₂Cl (14)

In a quartz flask equipped with magnetic stirrer (with an anchor coating of Teflon) and a reflux condenser linked to a bubble counter, were placed XeF₂ (1.7 g, 10 mmol) and 10 ml CH₂Cl₂. Then 5.0 g (19 mmol) of compound

TABLE 2
IR spectral data

Compounds (nc)	Frequency (cm^{-1})
4	2972 (C-H); 1644; 1520; 1464; 1382; 1292; 1266; 1092; 972; 896; 862; 812; 666; 500.
5	2964; 2908 (C-H); 1774 (FC=CF); 1680 (FC=CSi); 1376; 1298; 1260; 1214; 1080; 1054; 954; 852; 788.
6	2960; 2940; 2880 (C-H); 1772 (FC=CF); 1682 (FC=CGE); 1468; 1376; 1292; 1210; 1078; 1050; 950; 712; 586.
7	2972 (C-H); 1772 (FC=CF); 1684 (FC=CSi); 1646; 1520; 1496; 1476; 1466; 1408; 1382; 1302; 1216; 1054; 956.
8	2972 (C-H); 1774 (FC=CF); 1682 (FC=CSi); 1380; 1302; 1268; 1214; 1086; 1052; 958; 860; 848; 820; 790; 680.
9	2980; 2914 (C-H); 1772 (FC=CF); 1680 (FC=CSi); 1644; 1520; 1466; 1380; 1300; 1264; 1216; 1092; 1058; 974; 956; 864; 850; 812; 796; 680.
17	1682 (FC=CSi); 1387; 1354; 1340; 1307; 1239; 1184; 1150; 1132; 1036; 1003; 960; 895; 806; 818; 795; 450.
19	1690 (FC=CGe); 1338; 1308; 1244; 1212; 1178; 1156; 1136; 1080; 1032; 962; 882; 868; 852; 768; 732; 704; 668.

TABLE 3
Analytical data

Compounds (nc)	B.p. ($^{\circ}\text{C}$)	Found (%)			Formula
		Calculated (%)			
		C	H	F	
4	157-159	39.1	2.58	46.2	$\text{C}_8\text{H}_6\text{F}_6\text{Si}$
		39.3	2.46	46.7	
5	126-128	39.1	3.23	47.7	$\text{C}_9\text{H}_9\text{F}_7\text{Si}$
		38.8	3.24	47.8	
6	200	39.6	3.77	36.2	$\text{C}_{12}\text{H}_{15}\text{F}_7\text{Ge}$
		39.5	4.11	36.5	
7	134-136	33.6	2.01	54.0	$\text{C}_8\text{H}_6\text{F}_8\text{Si}$
		34.0	2.13	53.9	
8	223-225	36.4	1.34	57.0	$\text{C}_{14}\text{H}_6\text{F}_{14}\text{Si}$
		35.9	1.28	56.8	
9	236-240	38.8	1.41	53.1	$\text{C}_{14}\text{H}_6\text{F}_{12}\text{Si}$
		39.1	1.40	53.0	
17	99-102	39.1		69.0	$\text{C}_6\text{F}_{12}\text{Si}$
		22.0		69.5	
19	103-104	19.3		61.0	$\text{C}_6\text{F}_{12}\text{Ge}$
		19.3		61.2	

14 was added with a syringe while the mixture was cooled with cold water. The mixture was refluxed for 15 min, the solvent distilled off and the residue distilled to give 4.2 g (89%) of fluorodimethylsilylpentafluorobenzene (**4** (nc)).

*Fluorination of $C_6F_5GeBr_3$ (**10**)*

Compound **10** (5.3 g, 11 mmol) and 6 ml CH_2Cl_2 were placed in a Kel-F reactor and XeF_2 (2.8 g, 38 mmol) added in small portions with stirring. The dark red solution formed was stirred for 15 min at 25–30 °C. Distillation at reduced pressure gave 3.0 g (91%) of trifluorogermylpentafluorobenzene (**11**) [24].

*Fluorination of $C_6F_5GeCl_3$ (**12**)*

Method A

Compound **12** (6.8 g, 19.7 mmol), XeF_2 (5.1 g, 30 mmol) and 10 ml CH_2Cl_2 were treated as above to give 5.7 g of a 2:3.8:3:1 mixture of compounds $C_6F_5GeCl_3$, $C_6F_5GeCl_2F$, $C_6F_5GeClF_2$ and $C_6F_5GeF_3$ (^{19}F NMR data). The earlier unreported compounds $C_6F_5GeCl_2F$ and $C_6F_5GeClF_2$ were assigned to the following ^{19}F NMR signals (cf. with the spectra of $C_6F_5GeF_3$ and $C_6F_5GeCl_3$) (in $CDCl_3$):

$C_6F_5GeF_3$: 38.3 ($2F^{2,6}$); 22.6 ($1F^4$); 5.91 ($2F^{3,5}$); 11.5 (GeF_3) ppm.

$C_6F_5GeClF_2$: 37.3 ($2F^{2,6}$); 21.4 ($1F^4$); 5.63 ($2F^{3,5}$); 27.0 ($GeClF_2$) ppm.

$C_6F_5GeCl_2F$: 36.3 ($2F^{2,6}$); 20.0 ($1F^4$); 5.04 ($2F^{3,5}$); 36.3 ($GeCl_2F$) ppm.

$C_6F_5GeCl_3$: 35.7 ($2F^{2,6}$); 18.8 ($1F^4$); 4.47 ($2F^{3,5}$) ppm.

Method B

To a solution of compound **12** (3.3 g, 9.5 mmol) in 3 ml CH_2Cl_2 , xenon difluoride (3.3 g, 19.4 mmol) was added in portions and the mixture heated for 2 h at 66 °C (bath). Distillation gave 2.0 g of a colourless fuming liquid containing $C_6F_5GeClF_2$ and $C_6F_5GeF_3$ (1:2.75) (^{19}F NMR data).

Method C

Compound **12** (3.0 g, 8.6 mmol) was placed in a quartz flask and then XeF_2 (2.9 g, 17 mmol) added with stirring. The temperature was raised to 160 °C (bath) over 30 min and a colourless liquid (which fumed in air) was distilled off (1.8 g). The liquid contained $C_6F_5GeF_3$ (**11**), $1-GeF_3 = 1,4-C_6F_7$ (**18**), $GeF_3-1,3-C_6F_7$ and $1-GeF_3C_6F_9$ (**19**) (7:3.5:1.7:1) (^{19}F NMR data).

Method D

Compound **12** (4.3 g, 12 mmol) and NbF_5 (3.0 g, 16 mmol) were placed in a quartz flask. The mixture was heated to 220–230 °C (bath) allowing the volatile products to distil off. The cooled distillate was filtered from NbF_5 and redistilled. This procedure gave 3.8 g (88%) of the starting germane **12** (b.p., 203–207 °C [25]).

*Fluorination of $C_6F_5SiCl_3$ (**13**)*

Method A

Compound **13** (7.0 g, 23 mmol), 10 ml CH_2Cl_2 and XeF_2 (5.9 g, 34 mmol) were refluxed for 15 min to afford 5.3 g of silane **13** containing

traces of $C_6F_5SiFCl_2$ which was assigned ^{19}F NMR signals at 36 ($2F^{2,6}$), 18.2 ($1F^4$), 3.5 ($2F^{3,5}$) and 32 ($SiFCl_2$) ppm.*

Method B

Compound **13** (4.0 g, 13.2 mmol) and NbF_5 (2.5 g, 13.3 mmol) were placed in a flask. The mixture was heated to 130–140 °C allowing the volatile products to distil off. The mixture was then heated to give 2.6 g (78%) of $C_6F_5SiF_3$ [24].

Method C

The quartz flask equipped with a thermometer, magnetic stirrer and bubbler was cooled in an argon atmosphere to -40 °C and NbF_5 (1.2 g, 6 mmol), SO_2FCl (13 ml) and compound **13** (3.0 g, 10 mmol) were placed in it. Then XeF_2 (5.1 g, 30 mmol) was added in small portions with stirring. The mixture was allowed to stand for 20 min at 8–10 °C, the volatile products recondensed *in vacuo* (18 Torr) into a cooled trap (-70 °C) and then distilled. This gave 1.6 g of a colourless liquid containing compounds **15** and **16** ($-1:2$) (^{19}F NMR data).

Fluorination of $C_6F_5SiF_3$

Method A

A Teflon reactor equipped with a magnetic stirrer and a bubbler was cooled in an argon atmosphere to -40 °C, and 1.26 g (5 mmol) of $C_6F_5SiF_3$ and 5 ml of SO_2FCl were placed in it. Then $XeF^+ NbF_6^-$ (2.40 g, 6.7 mmol) was added in small portions with stirring and the mixture heated for 1.5 h to 10–15 °C. The volatile products were recondensed *in vacuo* (10 Torr) into a trap (-70 °C). This gave 1.0 g of a liquid containing 2.4 mmol of compound **15** and presumably trifluorosilylheptafluoro-1,3-cyclohexadienes (^{19}F NMR data). Analysis: Found: C, 25.2; F, 65.0%. $C_6F_{10}Si$ requires: C, 24.8; F, 65.5%.

Method B

Addition of 1.20 g (7.0 mmol) of XeF_2 to 1.40 g (5.56 mmol) of $C_6F_5SiF_3$, 5 ml SO_2ClF and 0.25 g (1.4 mmol) of NbF_5 at -30 °C afforded 1.4 g of a product containing compound **15** (3.1 mmol) and $C_6F_7SiF_3$ (1 mmol) (^{19}F NMR data).

Method C

Heating $C_6F_5SiF_3$ (2.0 g, 7.9 mmol), XeF_2 (6.3 g, 17.6 mmol) and 5 ml SO_2FCl from -30 °C to 80 °C (bath) gave 1.7 g (65%) of 1-trifluorosilylnonafluorocyclohexene (**17**) (nc).

Reaction of NbF_5 with perfluorotrifluorosilylcyclohexadienes

A mixture consisting of perfluorotrifluorosilylcyclohexadienes obtained in the previous experiment (B) (0.5 g, 1.7 mmol), 0.5 g (2.6 mmol) of NbF_5

* $C_6F_5SiFCl_2$ has been described (b.p., IR spectrum and elemental analysis) but no ^{19}F NMR spectrum was given [26].

and 0.5 ml SO_2FCl was placed in a glass tube. The mixture was shaken for 8 h at room temperature, SO_2FCl distilled off and the residue recondensed *in vacuo* when 0.5 g of a 1:2 mixture of the starting compounds was obtained (^{19}F NMR data). Analysis: Found: C, 24.5; F, 65.0%. $\text{C}_6\text{F}_{10}\text{Si}$ requires: C, 24.8; F, 65.5%.

Fluorination of $\text{C}_6\text{F}_5\text{GeF}_3$ (**11**)

Method A

The reaction was performed in a similar fashion to the fluorination of $\text{C}_6\text{F}_5\text{SiF}_3$ (method A). Compound **11** (0.50 g, 1.68 mmol) was reacted with $\text{XeF}^+ \text{NbF}_6^-$ (0.72 g, 2.0 mmol) and 5 ml SO_2FCl to produce 0.4 g of a product containing compounds **11**, **18** and presumably trifluorogermylheptafluoro-1,3-cyclohexadiene (3:7:1) (^{19}F NMR data).

Method B

To a stirred mixture of compound **11** (6.0 g, 20 mmol) and XeF_2 (6.46 g, 38 mmol), SbF_3 (0.05 g, 0.3 mmol) was added at 10 °C. An exothermic reaction commenced immediately with vigorous liberation of gas. After 10–15 min, the volatile products were recondensed into a trap (–70 °C). This gave 4.7 g of a mixture of 1-trifluorogermylheptafluoro-1,4-cyclohexadiene (**18**) (nc) and 1-trifluorogermynonafluorocyclohexene (**19**) (nc) (2:1) (^{19}F NMR data).

Fluorination of compound **18**

A mixture of compounds **18** and **19** (4.3 g) obtained in the previous experiment and 50 mg of SbF_3 were placed in a quartz flask provided with a magnetic stirrer and a reflux condenser with a bubbler. Then XeF_2 (2.0 g) was added in small portions. After the reaction was complete (3–5 min), the reaction mixture was cooled, the liquid separated from the solid residue and distilled in a quartz apparatus under a dry argon atmosphere. This gave a colourless liquid which fumed strongly in air. The yield of 1-trifluorogermynona-fluorocyclohexene (**19**) (nc) was 3.0 g (65%).

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