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REACTIONS OF POLYFLUOROARYL BROMIDES AND IODIDES WITH C-, Si-, Ge-, Sn- AND Pb-ELECTROPHILES AND TRIS(DIALKYLAMINO)PHOSPHINES[1]

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SUMMARY

The reactions of polyfluoroaryl bromides Ar_FBr or iodides Ar_FI with $P(NR'_2)_3$ and R_3MX (R = alkyl; M = Si, Ge, Sn, and Pb; X = Cl, Br) led to the formation of Ar_FMR_3. The reactions of C_6F_5Br with $P(NEt_2)_3$ and C-electrophiles (CH_3I, $C_6F_5CF_3$ and $(CF_3)_2C{=}CFC_2F_5$) gave the products of pentafluorophenylation of these substrates.

INTRODUCTION

In 1980 Marchenko and his co-workers reported the synthesis of CX_3SiMe_3 (X=Cl, Br) and CCl_3SiMe_2Cl by the reaction of CX_4 with $P(NR'_2)_3$ and methylchlorosilanes Me_3SiCl or Me_2SiCl_2 [2]. More recently, Ruppert and co-authors [3-6] showed that CF_3Br and perchlorofluoromethanes react with $P(NEt_2)_3$ and alkylchlorosilanes to form (perhalomethyl)alkylsilanes. Electrophiles may also include trimethylsilyl azide, trimethylsilyl thiocyanate [7], alkyl- and arylhalides of germanium, tin, lead, arsenic, selenium [6], phosphorus [6-11], perfluorinated olefins, octafluorotoluene [12], aroyl chlorides [13] and benzaldehyde [14]. However, all these reactions were performed using perhaloalkanes [7,11,13] or trihalomethanes [15,16]. Only Ruppert has mentioned in ref. [6] the possibility to carry out pentafluorophenylation using bromopentafluorobenzene and $P(NEt_2)_3$ but he did not give any particular examples. In the context of our research on the synthesis and reactivity of polyfluoroaromatic derivatives of the IV Main Group elements, we have studied the reactions of polyfluoroaryl bromides and iodides with $P(NR'_2)_3$ and alkyl halo derivatives of silicon, germanium, tin and lead, as well as some C-electrophiles.

RESULTS AND DISCUSSION

Treatment of a mixture of bromopentafluorobenzene **1** and chlorotrimethylsilane with an equimolar amount of tris(diethylamino)phosphine in pentane or hexane at room temperature led to trimethylsilylpentafluorobenzene 2 and precipitation of the phosphonium salt.

$$\underset{\mathbf{1}}{C_6F_5Br} + ClSiMe_3 + P(NEt_2)_3 \longrightarrow \underset{\mathbf{2}}{C_6F_5SiMe_3} + P(NEt_2)_3BrCl$$

Varying the reaction temperature (0-70 °C) and duration (1-4 h) did not change the yield of compound 2. The solvent effect was much more pronounced: under the same conditions (20 - 22 °C, 1 h) the yield of silylbenzene 2 decreased from 63-68 % (pentane, hexane, dichloromethane) to ~30 % (benzene, acetonitrile) (Table 1).

Substitution of tris(diethylamino)phosphine with tris(dimethylamino)phosphine or tris(dibutylamino)phosphine led to a slightly decreased yield of the target product 2. At the same time, attempts to replace $P(NR'_2)_3$ with triphenylphosphine or triethylphosphite were unsuccessful. It should be noted that inertness of pentafluorobenzene derivatives C_6F_5R (R = H, F, Cl, Br, OCH_3 [17], CN, C_6F_5 [18], CF_3, NO_2, H [19]) towards $P(OEt)_3$ at room temperature had been observed earlier. Only prolonged heating above 100 °C gives the products of phosphorylation of polyfluoroarenes (the Arbuzov reaction). On the other hand, pentafluoropyridine, octafluorotoluene and methylpentafluorobenzoate react with $P(NEt_2)_3$ in ether at 0-20 °C to form the respective perfluorinated 4,4'-biaryls, whereas the less electrophilic pentafluorobenzene and hexafluorobenzene do not react with $P(NEt_2)_3$ even when boiled in benzene [20]. In our experiments, the compounds $C_6F_5MR_3$ (MR_3 = $SiMe_3$, $GeEt_3$) did not change in the presence of $P(NEt_2)_3$ or the $P(NEt_2)_3$-$P(NEt_2)_3ClBr$ mixture, though $C_6F_5SnMe_3$ was slowly transformed in the presence of $P(NEt_2)_3$ to C_6F_5H (20 °C).

Pentafluorophenylation of chlorotrimethylsilane with bromopentafluorobenzene in the presence of $P(NEt_2)_3$ provided suitable model for the preparation of the respective derivatives of germanium, tin and lead. Bromotriethylgermane and chlorotriethylgermane are easily arylated at room temperature, forming triethylgermylpentafluorobenzene **3** in the 54-73 % yield. The yields of trimethylstannylpentafluorobenzene **4** and trimethylplumbylpentafluorobenzene **5** were somewhat lower. The length of unbranched alkyl chain does not affect the outcome of the reaction, as illustrated by the preparation of tributylstannylpentafluorobenzene **6** from C_6F_5Br, $BrSnBu_3$ and $P(NEt_2)_3$ in the 67 % yield.

$$C_6F_5Br + R_3MX + P(NEt_2)_3 \longrightarrow \underset{\mathbf{3-6}}{C_6F_5MR_3} + P(NEt_2)_3BrX$$

M = Ge R = Et X = Cl, Br **3**; M = Sn R = Me X = Cl **4**;

M = Sn R = Bu X = Br **6**; M = Pb R = Me X = Cl **5**

A preparatively significant aspect of this reaction is the effect of substituents in the aromatic ring on the reactivity of the aryl bromide. Substitution of the fluorine atom in the 4-position of bromopentafluorobenzene by the CN group only slightly affects the yield of the arylation product **10** of chlorotriethylgermane as compared to the yield of the corresponding pentafluorophenyl derivative **3**. But increased electron-donating character of substituent R in aryl bromide $4\text{-}RC_6F_4Br$ results in the lower reaction rate and/or decreased yield of the target product. This is exemplified by syntheses of compounds **11** and **12**.

$$\underset{\mathbf{7-9}}{4\text{-}R\text{-}C_6F_4Br} + ClGeEt_3 + P(NEt_2)_3 \longrightarrow \underset{\mathbf{10-12}}{4\text{-}RC_6F_4GeEt_3} + P(NEt_2)_3ClBr$$

R = CN(**7**, **10**), PrO(**8**, **11**), $C_5H_{10}N$(**9**, **12**)

TABLE 1

Reactions of 4-R-C_6F_4Br with R_3MX and $P(NEt_2)_3$

Ar_FBr mmol	R_3MX mmol	$P(NEt_2)_3$ mmol	Solvent ml	Time h	Yield %
1	Me_3SiCl		pentane		
50	55	55	120	1	2 63
1	Me_3SiCl		hexane		
50	50	50	120	1	2 67
1[1]	Me_3SiCl		hexane		
50	50	50	120	1	2 50
1[2]	Me_3SiCl		pentane		
25	25	25	60	1	2 51
1	Me_3SiCl		pentane		
25	25	25	60	4	2 44
1[3]	Me_3SiCl		CH_2Cl_2		
50	50	50	120	1	2 68
1	Me_3SiCl		ether		
50	50	50	120	1	2 40
1[3]	Me_3SiCl		THF		
50	50	50	120	1	2 39
1	Me_3SiCl		benzene		
50	50	50	120	1	2 32
1[3]	Me_3SiCl		MeCN		
50	50	50	120	1	2 29
1	Me_3SiCl	$P(NMe_2)_3$	pentane		
25	25	25	65	1	2 40
1	Me_3SiCl	$P(NBu_2)_3$	pentane		
50	50	50	150	1	2 40
1[4]	Et_3GeCl		pentane		
24	24	24	50	1	3 54

(continued)

TABLE 1 (cont.)

1	Et_3GeBr		pentane		
150	150	185	390	1	**3** 73
1	Me_3SnCl		pentane 100		
50	50	54	ether 30	0.25	**4** 50
1	Bu_3SnBr		pentane		
50	50	50	110	1	**6** 67
8	Et_3GeCl		pentane		
42	42	42	100	3	**11** 47
9	Et_3GeCl		pentane		**9**[5,6] 88
32	32	32	100	4	**12**[7] 44
9	Me_3SnCl		pentane		**9**[5] 56
16	16	16	50	4	**13** 40
14	Me_3SiCl		pentane		
19	20	20	50	2.5	**15** 68
14	Me_3SiCl		pentane		**15** 38
19	50	50	50	3	**17** 14
14[3]	Et_3GeCl		CH_2Cl_2		
30.5	40	35	30	1	**16** 52
15[1]	Et_3GeBr		hexane		
5	12.5	12.5	50	3	**18** 64

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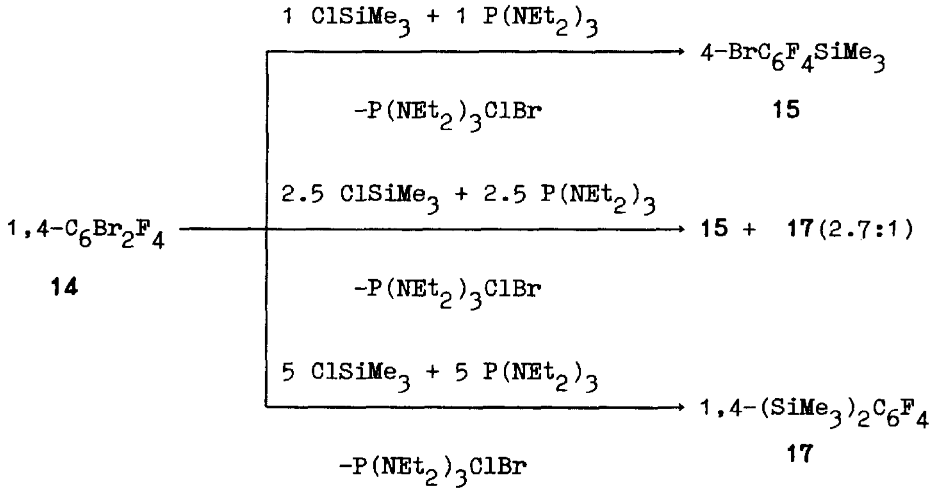
[1] At 70 °C [2] At 0 °C [3] After the reaction the solvent was distilled off at reduced pressure, the residue extracted with pentane (3x30 ml), pentane distilled off, the mixture was passed through a short Al_2O_3 column and the residue distilled in vacuum [4] After the solvent has been distilled off, the residue was steam distilled, the organic layer dried with $CaCl_2$ and distilled. [5] Conversion of the substrate [6] The products include 3-piperidino-1,2,4,5-tetrafluorobenzene, yield 20 % [7] Yield for the changed substrate.

A similar picture was observed in the arylation of chlorotrimethylstannane by 1-bromo-4-piperidinotetrafluorobenzene **9** which gave after 4 h 1-trimethylstannyl-4-piperidinotetrafluorobenzene **13** and the starting substrate **9** (56 % conversion), whereas C_6F_5Br was practically completely converted to stannylbenzene **4** in less than 1 h.

Bromobenzene, 4-fluorobromobenzene and 3-bromobenzotrifluoride did not react with $ClSiMe_3$ in the presence of $P(NEt_2)_3$.

Due to the deactivating influence of electron-donating substituents R in aryl bromides $4\text{-}RC_6F_4Br$ on the arylation rate, substitution of bromine in 1,4-dibromotetrafluorobenzene **14** by the trimethylsilyl and subsequently by the triethylgermyl groups has been carried out. Treatment of fluorinated dibromobenzene **14** with one equivalent of $ClSiMe_3$ or $ClGeEt_3$ and one equivalent of $P(NEt_2)_3$ gave 1-trimethylsilyl-4-bromotetrafluorobenzene **15** or 1-triethylgermyl-4-bromotetrafluorobenzene **16** respectively. Increased amount of $ClSiMe_3$ and $P(NEt_2)_3$ to 2.5 equivalents per one equivalent of dibromobenzene **14** led to the formation of a mixture of products of substitution of one and two bromine atoms by the $SiMe_3$ groups. In a large excess of chlorotrimethylsilane and $P(NEt_2)_3$ in boiling hexane, only 1,4-bis(trimethylsilyl)tetrafluorobenzene **17** was formed.



The reaction of bromine-containing silylbenzene **15** and germylbenzene **16** with $P(NEt_2)_3$, bromotriethylgermane, or chlorotrimethylsilane respectively gave 1-trimethylsilyl-4-triethylgermyltetrafluorobenzene **18**. This compound was also obtained by germylation of 4-lithio-1-trimethylsilyl-2,3,5,6-tetrafluorobenzene with chlorotriethylgermane.

$$\left.\begin{array}{l} 4\text{-}BrC_6F_4SiMe_3 + BrGeEt_3 \\ 4\text{-}BrC_6F_4GeEt_3 + ClSiMe_3 \end{array}\right] \xrightarrow[-\ P(NEt_2)_3XBr]{P(NEt_2)_3} \underset{\mathbf{18}}{1\text{-}SiMe_3\text{-}4\text{-}GeEt_3C_6F_4}$$

An attempt to perform the stepwise pentafluorophenylation of dimethyldichlorosilane proved to be less successful. With the ratio **1** : $P(NEt_2)_3$: Cl_2SiMe_2 = 1:1:1, the products were chlorodimethylsilylpentafluorobenzene **19** and bis(pentafluorophenyl)-dimethylsilane **20** (yields 2 and 60 % respectively). When the relative amount of dimethyldichlorosilane was increased six-fold, the yield of compound **19** slightly increased, but the main product remained to be tetraorganylsilane **20**.

$$C_6F_5Br + Me_2SiCl_2 \xrightarrow[-P(NEt_2)_3ClBr]{P(NEt_2)_3} \underset{\mathbf{19}}{C_6F_5SiMe_2Cl} + \underset{\mathbf{20}}{(C_6F_5)_2SiMe_2}$$

The predominant formation of compound **20** may be attributed to increased mobility of the halogen atom in $C_6F_5SiMe_2Cl$ as compared with that in Me_2SiCl_2 (cf. [21]).

Polyfluoroaryl bromides in the reactions with $P(NEt_2)_3$ and halides R_3SiX may be substituted by polyfluoroaryl iodides. Iodopentafluorobenzene and 4-iodoheptafluorotoluene **21** treated with chlorotrimethylsilane and $P(NEt_2)_3$ were readily transformed to the respective trimethylsilylarenes **2** and **22**.

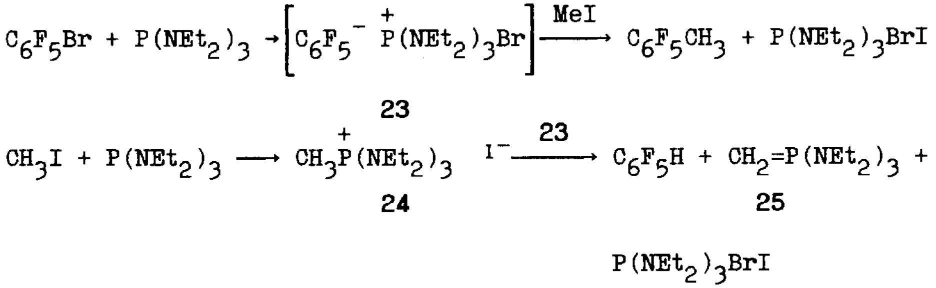
$$4\text{-}IC_6F_4R + Me_3SiCl + P(NEt_2)_3 \longrightarrow 4\text{-}Me_3SiC_6F_4R + P(NEt_2)_3ICl$$

$$\begin{array}{l} \mathbf{2}\ (R = F) \\ \mathbf{22}\ (R = CF_3) \end{array}$$

Chloropentafluorobenzene remained unchanged in these conditions.

In addition to synthesis of polyfluoroaromatic derivatives of Si, Ge, Sn and Pb, we have carried out pentafluorophenylation of some C-electrophiles and thus shown the utility of the reaction for the preparation of polyfluoroaryl derivatives of all the IV Main Group elements.

Bromopentafluorobenzene reacts with iodomethane and $P(NEt_2)_3$ to form 2,3,4,5,6-pentafluorotoluene and pentafluorobenzene in yields 20 and 32 % respectively. In the reaction mixture, concurrent processes of formation of phosphonium salts **23** and **24** seem to occur. The former salt can arylate iodomethane and, being a strong base [$pK_a(C_6F_5H)$ = 23 [22]], it can also react with the salt **24**, giving pentafluorobenzene and, possibly, ylide **25**. According to the data reported in ref.[23], ylides of such type are weaker nucleophiles than methylenetriphenylphosphorane and do not markedly react with polyfluoroaromatics in these conditions (cf. [24]).

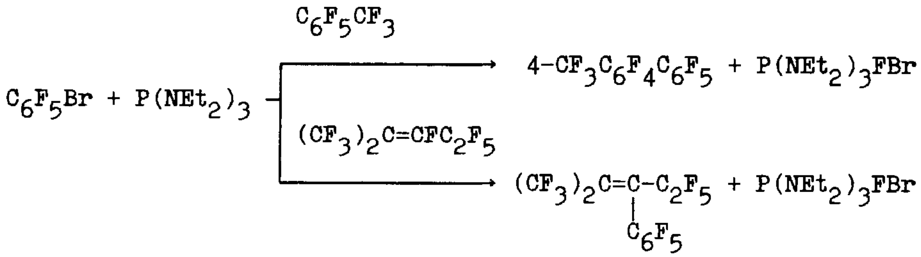


$$C_6F_5Br + P(NEt_2)_3 \rightarrow \underset{\mathbf{23}}{\left[C_6F_5^-\ \overset{+}{P}(NEt_2)_3Br\right]} \xrightarrow{MeI} C_6F_5CH_3 + P(NEt_2)_3BrI$$

$$CH_3I + P(NEt_2)_3 \longrightarrow \underset{\mathbf{24}}{CH_3\overset{+}{P}(NEt_2)_3}\ I^- \xrightarrow{\mathbf{23}} C_6F_5H + \underset{\mathbf{25}}{CH_2{=}P(NEt_2)_3} + P(NEt_2)_3BrI$$

It should be noted that the ability of bromopentafluorobenzene to be converted to pentafluorobenzene in the presence of $P(NEt_2)_3$ and a source of H^+ (water) has been shown by a special experiment.

Using $P(NEt_2)_3$, we have managed to carry out pentafluorophenylation of perfluorinated aromatic compounds and olefins. In the presence of $P(NEt_2)_3$, bromopentafluorobenzene arylates octafluorotoluene and perfluoro-2-methylpentene-2, giving perfluoro-4-methylbiphenyl and perfluoro-2-methyl-3-phenylpentene-2 respectively.



EXPERIMENTAL

The NMR spectra were recorded on the Bruker WP 200 SY and AC 200 instruments (^{1}H at 200 MHz, internal standard TMS; ^{19}F at 188.3 MHz, internal standard C_6F_6) (≃10 % $CDCl_3$ solutions). The IR spectra were recorded on a Specord M 80 instrument in a thin layer. The GLC analysis was carried out on an LKhM-72 chromatograph (15 % SE-30 or SKTFV-803 on the Chromosorb W, programmed heating, column 400x0.2 mm). Known compounds were identified by GLC and the NMR spectra by comparison with authentic samples. Syntheses using $P(NEt_2)_3$ were performed in dry argon atmosphere.

Table 2 and Table 3 present the NMR and IR spectral data of new compounds respectively, and Table 4 lists boiling (melting) temperatures and analytical data.

1-Bromo-4-propoxytetrafluorobenzene 8 (nc)

To a solution of 183 g-atom of sodium in 150 ml of anhydrous propanol was added 158 mmol of bromopentafluorobenzene. The mixture was refluxed for 6.5 h, then cooled, poured into 0.8 l of 5 % HCl, and extracted with dichloromethane. The extract was dried over $CaCl_2$, the solvent distilled off and the residue distilled in vacuum to give 24 g (53 %) of compound **8**.

1-Bromo-4-piperidinotetrafluorobenzene 9 (nc)

A solution of 120 mmol of bromopentafluorobenzene and 300 mmol of piperidine in 100 ml of ethanol was refluxed for 9 h. The solution was then cooled, poured into 0.5 l of 10 % HCl, the organic layer was separated and the aqueous layer extracted with

TABLE 2

NMR spectral data

Compound (nc)	^{1}H (ppm)	^{19}F (ppm)	
		F^{2,6}	F^{3,5}
6[1]	1.52(CH_2), 1.33-1.20($2CH_2$), 0.87(CH_3)	41.4	1.39
8	4.13(OCH_2), 1.78(CH_2), 1.00(CH_3)	27.3	6.56
9	3.18(4H), 1.65(6H)	25.6	12.2
10	1.10($GeEt_3$)	38.3	29.3
11	4.16(OCH_2), 1.78(CH_2), 1.15-0.99(CH_3, $GeEt_3$)	33.6	5.40
13	3.16(4H), 1.61(6H), 0.41($SnMe_3$)	37.3	11.8
15	0.40($SiMe_3$)	35.5	28.2
16	1.10($GeEt_3$)	36.4	28.4
18	1.08($GeEt_3$), 0.38($SiMe_3$)	33.5	(AA'BB')
21[2]		23.6	44.7
22[3]	0.42($SiMe_3$)	21.4	36.3

[1] δ(F): 9.03(F^4) [2] δ(F): 105.1(CF_3) [3] δ(F): 105.5(CF_3)

ether (100 ml). The combined extracts were washed with water, dried over $CaCl_2$ and the solvent was distilled off. Recrystallization from ethanol gave 21 g (84 %) of compound **9**.

4-Iodoheptafluorotoluene 21 (nc)

To a stirred suspension of 30 mmol of Ag_2O in 280 ml of iodomethane, 20 mmol of 4-hydrazoheptafluorotoluene was added in portions. The mixture was refluxed with stirring for 40 min, then filtered and the excess of iodomethane was distilled off. The residue was distilled in vacuum to give 23 g (33 %) of product **21**.

Chlorodimethylsilylpentafluorobenzene 19

A mixture of 57 mmol of $C_6F_5SiMe_2OEt$, 10 mmol of $C_6F_5SiMe_2Cl$ (see [25]) and 0.2 g of anhydrous zinc chloride in 75 ml of AcCl was stirred for 2 h at 20 °C. Vacuum distillation gave 11 g (74 %) of silylbenzene **19**, b.p. 40-45 °C at 3 mm Hg (lit. 95 °C at 32 mm Hg [26]).

Trimethylsilylpentafluorobenzene 2

A. a typical procedure . Bromopentafluorobenzene, chlorotrimethylsilane and pentane were placed into a three-necked flask provided with a dropping funnel, a stirrer and a reflux condenser with a calcium chloride tube. Then a solution of $P(NEt_2)_3$ in an equal volume of pentane was added dropwise with stirring in dry argon atmosphere. The mixture was stirred for 1 h at 20-22 °C, then filtered and the solvent was distilled off at reduced pressure. The residue was filtered if necessary, and vacuum distillation gave compound **2** [27].

The reactions of all aryl bromides with R_3MX and $P(NEt_2)_3$, as well as the reactions of aryl bromide **1** with $ClSiMe_3$ and $P(NR'_2)_3$ (R'= Me, Bu) were performed in a similar way. The reaction products **3** [28], **4** [29], and **12** [30] were described earlier.

B. To a solution of 50 mmol of iodopentafluorobenzene and 50 mmol of chlorotrimethylsilane in 100 ml of dichloromethane, a solution of 50 mmol of $P(NEt_2)_3$ in 15 ml of dichloromethane was added. The mixture was stirred for 1 h at 20-22 °C, the solvent was distilled off at reduced pressure, the residue extracted with pentane and the solvent distilled off. Vacuum distillation gave 5.6 g (46 %) of compound **2**.

Similarly, 19.8 mmol of 4-iodoheptafluorotoluene **21**, 26.7 mmol of Me_3SiCl and 23.5 mmol of $P(NEt_2)_3$ in 13 ml of dichloromethane were refluxed for 0.5 h to give 4.2 g (73 %) of 4-trimethylsilylheptafluorotoluene **22** (nc).

TABLE 3

Infrared spectral data

Compound (nc)	Frequency, cm^{-1}
6	2964, 2872, 2864, 2856(C-H), 1636, 1512, 1466, 1420, 1378, 1368, 1360, 1292, 1272, 1210, 1184, 1158, 1078, 1056, 1024, 962, 876, 868, 780, 696, 674, 606, 512
8	2972, 2908, 2884(C-H), 1632, 1512, 1508, 1502, 1390, 1348, 1280, 1156, 1148, 1114, 1056, 1046, 992, 962, 952, 944, 932, 910, 834, 768
9[1]	2940, 2848(C-H), 1632, 1486, 1452, 1384, 1226, 1106, 1004, 972, 876, 836, 784
10	2960, 2908, 2876(C-H), 2244(C≡N), 1636, 1466, 1400, 1382, 1278, 1256, 1228, 1010, 962, 832, 786, 714, 618
11	2956, 2920, 2908, 2892, 2876(C-H), 1638, 1494, 1484, 1448, 1388, 1376, 1368, 1348, 1264, 1210, 1154, 1096, 1014, 968, 940, 714, 708
13	2936, 2852(C-H), 1636, 1604, 1540, 1504, 1472, 1468, 1452, 1384, 1228, 1168, 1156, 1100, 1000, 952, 944, 900, 778, 712, 540
15	2960, 2904(C-H), 1626, 1490, 1480, 1440, 1420, 1416, 1382, 1368, 1258, 1236, 1024, 994, 950, 934, 922, 848, 792, 788, 772, 720, 700, 634, 586, 500
16[2]	2956, 2936, 2908, 2876(C-H), 1452, 1444, 1440, 1380, 1228, 1022, 944, 900, 590
18	2960, 2908, 2876(C-H), 1420, 1396, 1254, 1226, 1014, 976, 952, 934, 916, 840, 770, 632, 590, 544, 436
21[2]	1641, 1485, 1400, 1323, 1196, 1176, 1154, 975, 920, 710
22	2964, 2908(C-H), 1656, 1596, 1516, 1456, 1420, 1322, 1274, 1258, 1182, 1150, 970, 948, 936, 850, 796, 772, 748, 736, 712, 632

[1] At KBr [2] At CCl_4

1-Triethylgermyl-4-cyanotetrafluorobenzene 10 (nc)

A solution of 35 mmol of $P(NEt_2)_3$ in 10 ml of CH_2Cl_2 was added dropwise to a boiling solution of 31.5 mmol of 4-bromotetrafluorobenzonitrile [31] and 35 mmol of chlorotriethylgermane in 40 ml of dichloromethane. The mixture was refluxed with stirring for 40 min, then cooled, the solvent was distilled off at reduced pressure, the residue was treated with 8 ml of conc. HCl and extracted with dichloromethane. The extract was dried over the mixture of K_2CO_3 and $CaCl_2$ and the solvent was distilled off. Distillation in vacuum afforded 6.2 g (59 %) of compound **10**.

Trimethylplumbylpentafluorobenzene 5

To a boiling solution of 50 mmol of **1** and 55 mmol of Me_3PbCl in 200 ml of dichloromethane was added with stirring a solution of 55 mmol of $P(NEt_2)_3$ in 20 ml of CH_2Cl_2. The mixture was then stirred for 2 h at 22-25 °C, the solvent was distilled off, the dark residue was extracted with hexane (3x200 ml), the solvent was distilled off at reduced pressure and the residue distilled in vacuum to give 9.4 g (45 %) of compound **5**, b.p. 90-92 °C at 4 mm Hg (lit. 40-45 °C at 0.01 mm Hg [32]).

1,4-Bis(trimethylsilyl)tetrafluorobenzene 17

A solution of 100 mmol of $P(NEt_2)_3$ in 20 ml of hexane was added to a solution of 20 mmol of 1,4-dibromotetrafluorobenzene **14** and 100 mmol of chlorotrimethylsilane in 10 ml of hexane. The mixture was refluxed with stirring for 3 h, then cooled and filtered. After hexane was distilled off at reduced pressure, the residue was dissolved in 40 ml of CH_2Cl_2, then washed with 15 % HCl (2 x 40 ml), with water, and dried over $CaCl_2$. The solvent was distilled off, and the residue distilled in vacuum to give 2.0 g (35 %) of solid compound **17**, m.p. 52-53 °C (from MeOH) (lit. 53-55 °C [33]), b.p.100 °C at 13 mm Hg.

1-Trimethylsilyl-4-triethylgermyltetrafluorobenzene 18 (nc)

A. To a solution of 15 mmol of 1-trimethylsilyl-2,3,5,6-tetrafluorobenzene in 20 ml of ether was added, with cooling (-60 °C) and stirring during 20 min, 16 ml of 1.4 M BuLi in hexane. The suspension was stirred for 30 min, then a solution of 15 mmol of Et_3GeCl in 5 ml of ether was added to it dropwise. The temperature was raised during 1 h to room temperature, the reaction mixture was treated with 50 ml of 5 % HCl, the organic layer was washed with water, dried over $CaCl_2$, and the solvent distilled off. Vacuum distillation gave 2.3 g (35 %) of compound **18**.

B. A solution of 12 mmol of $P(NEt_2)_3$ in 5 ml of pentane was added dropwise to a stirred solution of 9.8 mmol of aryl bromide **16** and 15 mmol of chlorotrimethylsilane in 10 ml of pentane. As shown by the ^{19}F NMR data, after 2 h of stirring at 20 °C, the ratio of substrate **16** to product **18** was ~ 1:1. Pentane was distilled off and the residue was heated for 1 h at 40-45 °C. The mixture was cooled, applied to a short Al_2O_3 column and eluted with pentane. After the solvent has been distilled off, the oil that had separated was again passed through the Al_2O_3 column. Vacuum distillation gave 1.8 g (48 %) of product **18**.

Reaction of bromopentafluorobenzene 1 with $P(NEt_2)_3$ and dichlorodimethylsilane

A. The reaction of 50 mmol of bromopentafluorobenzene, 300 mmol of $SiMe_2Cl_2$ and 50 mmol of $P(NEt_2)_3$ in 120 ml of pentane was carried out according to a typical procedure. Vacuum distillation gave a mixture of 10 mmol of silane **20** and 3 mmol of silane **19** (yields 40 and 6 % respectively) (b.p.122 -124 °C at 7 mm Hg) (silane **20** boils at 140-144 °C at 14 mm Hg [34]).

B. Similarly, the reaction of 50 mmol of bromopentafluorobenzene, 50 mmol of dichlorodimethylsilane and 50 mmol of $P(NEt_2)_3$ afforded a mixture of 15 mmol of silane **20** and 1 mmol of silane **19** (yields 60 and 2 % respectively).

Reaction of C_6F_5Br with CH_3I and $P(NEt_2)_3$

According to a typical procedure, the reaction of 50 mmol of bromopentafluorobenzene, 100 mmol of iodomethane, 50 mmol of $P(NEt_2)_3$ in 120 ml of pentane led to a mixture of 1.82 g (20 %) of $C_6F_5CH_3$ and 2.65 g (32 %) of C_6F_5H (GLC data).

TABLE 4
Analytical data

Compound (no)	B.p. (°C at mm Hg)	Found/Requires, %					Formula
		C	H	F	Br	N	
6	157(6)	47.4	6.36	20.9			$C_{18}H_{15}F_5Sn$
		$\overline{47.3}$	$\overline{5.91}$	$\overline{20.8}$			
8	98-101(9)	37.9	2.38	26.6	28.3		$C_9H_7BrF_4O$
		$\overline{37.6}$	$\overline{2.44}$	$\overline{26.5}$	$\overline{27.9}$		
9	41-42[1]	42.5	3.42	24.8	25.6		$C_{11}H_{10}BrF_4N$
	(from EtOH)	$\overline{42.3}$	$\overline{3.20}$	$\overline{24.4}$	$\overline{25.6}$		
10	128-129(5)	46.9	4.40	22.3		4.41	$C_{13}H_{15}F_4GeN$
		$\overline{46.8}$	$\overline{4.50}$	$\overline{22.8}$		$\overline{4.20}$	
11	85-87(4)	49.1	6.07	21.2			$C_{15}H_{22}F_4GeO$
		$\overline{49.1}$	$\overline{6.00}$	$\overline{20.7}$			
13	116-120(7)	42.7	4.75	18.5		3.86	$C_{14}H_{19}F_4NSn$
	42-44[1]	$\overline{42.5}$	$\overline{4.80}$	$\overline{19.2}$		$\overline{3.54}$	
15	105-107(17)	36.1	3.03	24.8	27.0		$C_9H_9BrF_4Si$
		$\overline{35.9}$	$\overline{2.99}$	$\overline{25.2}$	$\overline{26.6}$		
16	122-125(5)	37.6	3.91	18.1	20.7		$C_{12}H_{15}BrF_4Ge$
		$\overline{37.2}$	$\overline{3.87}$	$\overline{18.7}$	$\overline{20.6}$		
18	128-130(5)	47.5	6.50	19.2			$C_{15}H_{24}F_4GeSi$
		$\overline{47.2}$	$\overline{6.29}$	$\overline{19.9}$			
21[2]	68-71(15)	24.5		39.0			C_7F_7I
		$\overline{24.4}$		$\overline{38.7}$			
22	51-52(6)	41.4	3.12	45.6			$C_{10}H_9F_7Si$
		$\overline{41.4}$	$\overline{3.10}$	$\overline{45.9}$			

[1] M.p. [2] Iodine: Found 36.6 %, requires 36.9 %

Perfluoro-4-methylbiphenyl

The reaction of 50 mmol of bromopentafluorobenzene, 150 mmol of octafluorotoluene, 50 mmol of $P(NEt_2)_3$ and 120 ml of pentane performed according to a typical procedure gave 9.5 g (50 %) of perfluoro-4-methylbiphenyl, b.p. 85 °C at 5 mm Hg (lit. m.p. 32-33 °C [35]).

Perfluoro-2-methyl-3-phenylpentene-2

Similarly, the reaction of 50 mmol of bromopentafluorobenzene, 80 mmol of perfluoro-2-methylpentene-2, 50 mmol of $P(NEt_2)_3$ and 100 ml of pentane afforded 13.5 g (64 %) of the product, b.p. 43-45 °C at 15 mm Hg (lit. 130-132 °C [36]).

Reaction of C_6F_5Br with H_2O and $P(NEt_2)_3$

A solution of 50 mmol of $P(NEt_2)_3$ in 20 ml of pentane was added to a mixture of 50 mmol of C_6F_5Br, 50 mmol of water and 100 ml of pentane. After 1 h, the precipitate was filtered off and the filtrate was distilled to give 2.85 g (34 %) of C_6F_5H.

Reaction of bromobenzene, 4-fluorobromobenzene and 3-bromobenzotrifluoride with $P(NEt_2)_3$ and $ClSiMe_3$

A solution of 50 mmol of aryl bromide and 47-54 mmol of chlorotrimethylsilane in 100 ml of pentane was treated with a solution of 55 mmol of $P(NEt_2)_3$ in 10-15 ml of pentane or ether. The mixture was stirred at 20-22 °C for 1 h (4-FC_6H_4Br, 3-$BrC_6H_4CF_3$) or 50 h (C_6H_5Br) and the solvent was distilled off at reduced pressure. Vacuum distillation afforded the starting aryl bromides in 84-90 % yields.

Reaction of chloropentafluorobenzene with $P(NMe_2)_3$ or $P(NEt_2)_3$ and $ClSiMe_3$

A solution of 46 mmol of $P(NMe_2)_3$ or $P(NEt_2)_3$ in 10 ml of pentane was added dropwise with stirring to a solution of 40 mmol of chloropentafluorobenzene and 46 mmol of chlorotrimethylsilane in 40 ml of pentane. The mixture was stirred for 1 h at 20-22 °C, the yellow solution was carefully treated with 20 ml of conc.

HCl, the organic layer was washed with water, dried over $CaCl_2$ and the solvent was distilled off. As shown by GLC and NMR, the residue contains chloropentafluorobenzene in addition to $(SiMe_3)_2O$ and pentane (recovery 91-94 %).

Reaction of compounds 2, 3 and 4 with $P(NEt_2)_3$ and $P(NEt_2)_3BrCl$

In the NMR tube were placed 0.2-0.3 g of compound **2**, (**3** or **4**), 0.5 ml of pentane and 0.4 g of $P(NEt_2)_3$. The mixture was stirred and allowed to stand at 20-22 °C. According to ^{19}F NMR data, after 50 h compounds **1** and **2** remained unchanged, while $C_6F_5SnMe_3$ was slowly transformed to pentafluorobenzene ($C_6F_5SnMe_3 : C_6F_5H$ = 9:1). Treatment of these solutions with $(Et_2N)_3PClBr$ (20 °C, 2 h) did not lead to any changes in their ^{19}F NMR spectra.

Reaction of $P(OEt)_3$ with C_6F_5Br and Me_3SiCl

A solution of 50 mmol of $P(OEt)_3$ in 30 ml of pentane was added dropwise with stirring to a solution of 50 mmol of bromopentafluorobenzene and 50 mmol of Me_3SiCl in 100 ml of pentane. The mixture was stirred for 1 h, and the solvent was distilled off. As shown by ^{19}F NMR data, a single fluoroaromatic compound in the residue was bromopentafluorobenzene.

Reaction of PPh_3 with C_6F_5Br and Me_3SiCl

A solution of 65 mmol of PPh_3 in 50 ml of dichloromethane was added dropwise to a solution of 50 mmol of bromopentafluorobenzene, 65 mmol of Me_3SiCl in 100 ml of dichloromethane. The mixture was stirred for 1 h, the solvent distilled off, the residue extracted with pentane (2x20 ml), and pentane distilled off. According to ^{19}F NMR data, the residue contained only bromobenzene **1**.

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