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Reactions of pentafluorophenylxenon(II) hexafluoroarsenate $[C_6F_5Xe]^+[AsF_6]^-$ with aromatic compounds

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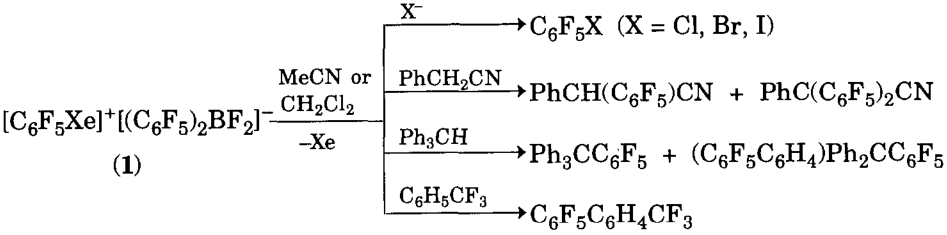
Abstract

Pentafluorophenylxenon(II) hexafluoroarsenate $[C_6F_5Xe]^+[AsF_6]^-$ reacts (MeCN, 20 °C) with aromatic compounds C_6H_5X ($X = CH_3$, F, CF_3, NO_2 and CN), yielding isomeric mixtures of polyfluorinated biphenyls $XC_6H_4C_6F_5$. When X = I, iodopentafluorobenzene is formed in addition, whereas trimethylsilylbenzene ($X = SiMe_3$) is only converted to $C_6H_5C_6F_5$ and C_6F_5H. These results are compared with the data for the radical pentafluorophenylation and fluorination reactions of the corresponding aromatic compounds with XeF_2. Polyfluoroaromatic compounds C_6F_6, C_6F_5H, C_6F_5I, C_6F_5CN and $C_6F_5SiMe_3$ do not react with $[C_6F_5Xe]^+[AsF_6]^-$ under the same conditions.

Introduction

Since the first communications on the synthesis of $[C_6F_5Xe]^+[Y]^-$ $\{Y = C_6F_5BF_3$ [1, 2], $(C_6F_5)_3BF$ [3] and $(C_6F_5)_2BF_2$ **1** [4]$\}$, only a few data have been available about their reactivity [1–7]. The reaction of **1** with nucleophiles X^- (X = Cl, Br and I) leads to halogenopentafluorobenzenes C_6F_5X [1, 2]. Interaction of salt **1** with C–H acids results in the replacement of the acidic proton by the C_6F_5 group. Substitution of the aromatically bonded hydrogen by the C_6F_5 group proceeds to a small extent, but the structure of the products has not yet been investigated [5–7].



$$\underset{(\mathbf{1})}{[C_6F_5Xe]^+[(C_6F_5)_2BF_2]^-} \xrightarrow[-Xe]{\text{MeCN or } CH_2Cl_2} \left| \begin{array}{l} \xrightarrow{X^-} C_6F_5X \ (X = Cl, Br, I) \\ \xrightarrow{PhCH_2CN} PhCH(C_6F_5)CN + PhC(C_6F_5)_2CN \\ \xrightarrow{Ph_3CH} Ph_3CC_6F_5 + (C_6F_5C_6H_4)Ph_2CC_6F_5 \\ \xrightarrow{C_6H_5CF_3} C_6F_5C_6H_4CF_3 \end{array} \right.$$

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However, the $[C_6F_5Xe]^+$ cation is able to arylate aromatic compounds. The information on isomer distribution in the pentafluorophenylated products could suggest the mechanism of the reaction. Unfortunately, thermal instability of $[C_6F_5Xe]^+[(C_6F_5)_2BF_2]^-$ [4] did not allow us to study the reactivity of the $[C_6F_5Xe]^+$ cation at room or elevated temperatures.

Hence, we have studied the interaction of aromatic compounds with $[C_6F_5Xe]^+[AsF_6]^-$ (**2**). This salt can easily be prepared from salt **1** [4] (details of the preparation are described elsewhere). Its solution in MeCN was stable at room temperature for *c.* 1 d, but quickly decomposed at 70–80 °C (3–4 h) to yield pentafluorobenzene and decafluorobiphenyl (~10:1, mol).

Results and discussion

Pentafluorophenylxenon(II) hexafluoroarsenate (**2**) reacts readily with toluene at room temperature in acetonitrile to yield xenon and a mixture of 2′-, 3′- and 4′-$CH_3C_6H_4C_6F_5$ (**3a, 3b, 3c**). No pentafluorobenzene or benzyl derivatives such as $C_6H_5CH_2C_6F_5$ were detected among the reaction products (Table 1). Interaction of salt **2** with fluorobenzene proceeds more slowly and gives isomeric hexafluorobiphenyls $FC_6H_4C_6F_5$ (**4a, 4b, 4c**). Very similar

TABLE 1

Reactions of $[C_6F_5Xe]^+[AsF_6]^-$ (**2**) with C_6H_5X (CH_3CN, RT)

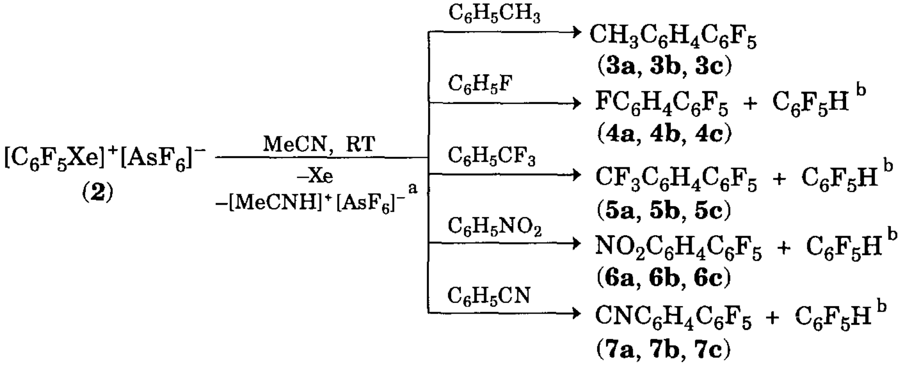
2 (μmol)	C_6H_5X (μmol)	Time (h)	Yield of C_6F_5H (%)	$XC_6H_4C_6F_5$ isomers (%)					
				Yield			Relative ratio[a]		
				2′-	3′-	4′-	2′-	3′-	4′-
45	$C_6H_5CH_3$ (76)	1.25	–	50	21	21	44	19	37
51	C_6H_5F (62)	14	5	35	20	24	37	19	44
12	$C_6H_5CF_3$ (25)	30	5	18	40	20	18	41	41
55	$C_6H_5NO_2$ (65)	42	trace	27	22.5	22.5	28	24	48
45	C_6H_5CN (62)	24	trace	35	31	26	30	26	44
55[b]	C_6H_5I (60)	1	6.3	11.1	7.5	11.6	26	18	56
53[c]	$C_6H_5SiMe_3$ (53)	1	29						

[a] Corrected for two *ortho* and two *meta* positions.

[b] Iodopentafluorobenzene (50% yield) and $C_6F_5C_6H_5$ (6.5% yield) were obtained.

[c] $C_6F_5C_6H_5$ (57% yield) and $FSiMe_3$ were obtained.

results were obtained in the reactions of salt **2** with benzotrifluoride, nitrobenzene and benzonitrile, but here the conversion was complete only after 24–42 h and small amounts of C_6F_5H were formed in addition to the corresponding isomeric biphenyls.



[a]During the reaction, the concentration of $[AsF_6]^-$ remained virtually unchanged.
[b]Traces or minor amounts.

The reaction of iodobenzene with salt **2** leads to a mixture of isomeric $IC_6H_4C_6F_5$ (**8a, 8b, 8c**). Small amounts of $C_6F_5C_6H_5$ and C_6F_5H are obtained, as well, but the main product is iodopentafluorobenzene. Examination of this process by ^{19}F NMR spectroscopy immediately after addition of C_6H_5I to the MeCN solution of **2** showed no formation of phenyl(pentafluorophenyl)iodonium salts as possible precursors of C_6F_5I. It should be emphasized that $[C_6F_5IC_6H_5]^+$ is relatively stable in MeCN at room temperature [8].

$$[C_6F_5Xe]^+[AsF_6]^- + C_6H_5I \xrightarrow[-Xe]{MeCN} C_6F_5I + \underset{\textbf{(8a, 8b, 8c)}}{IC_6H_4C_6F_5} + C_6F_5C_6H_5 + C_6F_5H$$

Interaction of salt **2** with trimethylsilylbenzene proceeds immediately after addition of the aromatic compound to the solution of salt **2**. 2,3,4,5,6-Pentafluorobiphenyl is the main product in addition to pentafluorobenzene, fluorotrimethylsilane and xenon.

$$[C_6F_5Xe]^+[AsF_6]^- + C_6H_5SiMe_3 \longrightarrow C_6F_5C_6H_5 + C_6F_5H + FSiMe_3$$

This regiospecificity of the pentafluorophenylation of $C_6H_5SiMe_3$ is not attributed to other trimethylsilylarenes: treatment of salt **2** with 1-trimethylsilyl-2-fluorobenzene or 1-trimethylsilyl-3-trifluoromethylbenzene leads to the formation of a mixture of pentafluorophenylated aromatics.

Comparison of the reactions of $[C_6F_5Xe]^+[AsF_6]^-$ in acetonitrile and of XeF_2/HF in CH_2Cl_2 or CCl_4 [9] with aromatic compounds indicates formally similar results: transfer of group Z from [Z–Xe] ($Z = C_6F_5$ or F) to C_6H_5X and generation of $Z-C_6H_4X$ and xenon. But the isomer ratio of $XC_6H_4C_6F_5$ ($X = CH_3$, F, CF_3 and NO_2) differs substantially from that of aryl fluorides which were obtained by the fluorination of C_6H_5X with XeF_2 [9]. In the latter case, the relative ratio of isomeric aryl fluorides FC_6H_4X demonstrates the preferential formation of *ortho-* and *para*-disubstituted benzenes ($X=CH_3$, F), whereas predominantly *meta* isomers were obtained from $C_6H_5CF_3$ and $C_6H_5NO_2$ (Table 2). (Unfortunately, our attempts to perform the reaction of salt **2** with fluorobenzene or benzotrifluoride in dichloromethane suspension failed, but in our opinion the observed difference between $XeF_2/HF{-}CH_2Cl_2$ (CCl_4) and $[C_6F_5Xe]^+[AsF_6]^-$–MeCN cannot be explained by the different solvent.) On the other hand, the composition of our products and the relative ratio of isomeric biphenyls $XC_6H_4C_6F_5$ ($X=CH_3$, F, NO_2, CF_3, CN) are in accordance with the products obtained in the pentafluorophenylation of C_6H_5X with C_6F_5 radicals (Table 3). At the same time, the different composition of the reaction mixtures derived from $[C_6F_5Xe]^+[AsF_6]^-$ and C_6H_5X ($X=CH_3$, F, CF_3, NO_2 and CN) on the one hand, and iodobenzene and trimethylsilyl-

TABLE 2

Reactions of C_6H_5X with XeF_2 [9]

C_6H_5X	FC_6H_4X (relative ratio, %)[a]					
	In CH_2Cl_2–HF			In CCl_4–HF		
	2-F	3-F	4-F	2-F	3-F	4-F
$C_6H_5CH_3$				35	6	59
C_6H_5F	16	4	80	15	4	81
$C_6H_5CF_3$	28	48	24	0	91	9
$C_6H_5NO_2$	20	55	25	18	53	29

[a] Corrected for two *ortho* and two *meta* positions.

TABLE 3

Reactions of C_6H_5X with C_6F_5 radicals

C_6H_5X	$XC_6H_4C_6F_5$ (relative ratio, %)[a]			Ref.
	2′-X	3′-X	4′-X	
$C_6H_5CH_3$	53	19	28	10
$C_6H_5CH_3$	49	25	26	11
$C_6H_5CH_3$	44	19	37	13
C_6H_5F	33	24	43	12
C_6H_5F	28	13	59	13
$C_6H_5CF_3$	18	46	36	[b]
C_6H_5CN	29	35	37	[b]
C_6H_5I	26	18	56	[b]
$C_6H_5NO_2$	17	42	41	10

[a] Corrected for two *ortho* and two *meta* positions.
[b] This work.

benzene on the other hand, has prompted us to study the unknown interaction of pentafluorophenyl radicals with C_6H_5I and $C_6H_5SiMe_3$.

Following the authors of refs. 10, 12 and 13, we used the reaction of pentafluoroaniline with pentyl nitrite for the generation of the C_6F_5 radical. Treatment of $C_6F_5NH_2$ with $C_5H_{11}ONO$ in an excess of iodobenzene causes spontaneous heating of the solution up to 70–80 °C and gas evolution. Analysis of the reaction mixture by ^{19}F NMR spectroscopy showed the presence of the same products as obtained earlier in the reaction of iodobenzene with pentafluorophenylxenon(II) hexafluoroarsenate.

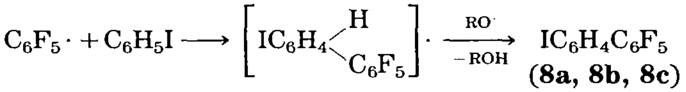
$$C_6F_5NH_2 + C_5H_{11}ONO + C_6H_5I \xrightarrow[\substack{-H_2O,\ -N_2,\\ -C_5H_{11}OH}]{} C_6F_5I + \underset{\textbf{(8a, 8b, 8c)}}{IC_6H_4C_6F_5} + C_6F_5H + C_6F_5C_6H_5$$

It should be noted that the isomer ratio of $IC_6H_4C_6F_5$ (**8a, 8b, 8c**) obtained here is the same as for the reaction of $[C_6F_5Xe]^+[AsF_6]^-$ with C_6H_5I.

The predominant formation of iodopentafluorobenzene may be explained by the attack of the electrophilic pentafluorophenyl radical [13] on C_6H_5I and subsequent decomposition of the unstable diaryliodonium radical [eqn. (2)]. The transfer of iodine to the more electronegative aryl group during decomposition of the unsymmetric radical $[RR'I]\cdot$ has been discussed in ref. 14. Furthermore, addition to the iodine atom of iodobenzene is the preferable direction of electrophilic attack under the kinetically controlled conditions [15]. The formation of other products may be represented by eqns. (3)–(5).

$$C_6F_5NH_2 + C_5H_{11}ONO \xrightarrow[-H_2O]{} [C_6F_5N_2^+ + C_5H_{11}O^-] \longrightarrow [C_6F_5N{=}NOC_5H_{11}] \longrightarrow C_6F_5\cdot + C_5H_{11}O\cdot + N_2 \tag{1}$$

$$C_6F_5\cdot + C_6H_5I \longrightarrow [C_6F_5IC_6H_5]\cdot \longrightarrow C_6F_5I + C_6H_5\cdot \tag{2}$$



$$C_6F_5\cdot + C_6H_5I \longrightarrow \left[IC_6H_4\!<\!\substack{H\\ C_6F_5}\right]\cdot \xrightarrow[-ROH]{RO\cdot} \underset{\textbf{(8a, 8b, 8c)}}{IC_6H_4C_6F_5} \tag{3}$$

$$C_6F_5\cdot + C_6H_5\cdot \longrightarrow C_6F_5C_6H_5 \tag{4}$$

$$C_6F_5\cdot + ROH \longrightarrow C_6F_5H + RO\cdot \quad (R{=}H,\ C_5H_{11}) \tag{5}$$

Generation of the $C_6F_5\cdot$ radical from $C_6F_5NH_2$ and $C_5H_{11}ONO$ in excess trimethylsilylbenzene leads to the formation of 2,3,4,5,6-pentafluorobiphenyl and pentafluorobenzene, together with some pentafluoroaniline derivatives.

$$C_6F_5NH_2 + C_5H_{11}ONO + C_6H_5SiMe_3 \xrightarrow[\substack{-H_2O,\ -N_2,\\ -C_5H_{11}OH}]{} C_6F_5C_6H_5 + C_6F_5H + \ldots$$

In order to fill in the gap in the literature, we have also carried out the radical pentafluorophenylation of $C_6H_5CF_3$ and C_6H_5CN. The results (Table

3) are in a good agreement with our data on the pentafluorophenylation of these aromatics with salt **2** (Table 1).

It is known that hexafluorobenzene does not react with pentafluorophenyl radicals produced from pentafluoroaniline and pentyl nitrite at 80 °C [10], whereas pentafluorobenzene [11] or 1,2,4,5-tetrafluorobenzene [16] are very slowly converted to deca- and nona-fluorobiphenyls, respectively.

To complete the investigation of the reaction of $[C_6F_5Xe]^+[AsF_6]^-$ with aromatic compounds, we have studied the interaction of salt **2** with polyfluoroaromatics. We have found that C_6F_6, C_6F_5H, C_6F_5CN, $C_6F_5SiMe_3$ and C_6F_5I are inert towards $[C_6F_5Xe]^+[AsF_6]^-$. No reaction was observed between $[C_6F_5Xe]^+[BF_4]^-$ and C_6F_5I in boiling acetonitrile, as well. This result contradicts that in ref. 3 which reports formation of the $[(C_6F_5)_2I]^+$ salt on treatment of C_6F_5I with $[C_6F_5Xe{-}MeCN]^+[(C_6F_5)_3BF]^-$. It should be noted that the salt $[C_6F_5Xe]^+[(C_6F_5)_3BF]^-$ was not isolated as an individual substance [3]. Hence, the formation of the iodonium salt $[(C_6F_5)_2I]^+$ may possibly be explained by the reaction of C_6F_5I with the initial XeF_2 which remains in the reaction mixture. Actually, we have found out that XeF_2 can convert iodopentafluorobenzene via $C_6F_5IF_2$ in the presence of acidic C_6F_5BXY compounds to the corresponding iodonium salt. (The conversion of $C_6F_5IF_2$ to $[(C_6F_5)_2I]^+$ has also been demonstrated in ref. 3.)

$$C_6F_5I + XeF_2 \longrightarrow C_6F_5IF_2 \xrightarrow{B(C_6F_5)_3} [(C_6F_5)_2I]^+[(C_6F_5)_3BF]^-$$

The inertness of the pentafluorobenzene derivatives C_6F_5X towards salt **2** is contrary to the easy fluorination of these compounds by $XeF_2{-}BF_3\cdot OEt_2$ which produces 1-X-heptafluoro-1,4-cyclohexadienes (X = F, H [17], $SiMe_3$ [18]). We have found that XeF_2 reacts with iodopentafluorobenzene in CH_2Cl_2 in the presence of catalytic amounts of $BF_3\cdot OEt_2$ in the same manner as in the absence of a Lewis acid or a solvent [19].

$$C_6F_5I + XeF_2 \xrightarrow[CH_2Cl_2]{[BF_3\cdot OEt_2]} C_6F_5IF_2 + Xe$$

The results obtained have encouraged us to the conclusion that the pentafluorophenyl radical is a reactive key intermediate which participates in the reaction of $[C_6F_5Xe]^+[AsF_6]^-$ with aromatic compounds. The mechanism of the generation of this species from salt **2** is being examined at present.

The synthesis of individual fluorinated biphenyls for identification of the products produced in the reaction of $[C_6F_5Xe]^+[AsF_6]^-$ with C_6H_5X was performed by the following principal methods:

$$XC_6H_4Br + BuLi \longrightarrow XC_6H_4Li \xrightarrow{C_6F_6} XC_6H_4C_6F_5$$

[X = 2-CH_3 (**3a**), 3-CH_3 (**3b**), 4-CH_3 (**3c**), 3-CF_3 (**5b**), 4-CF_3 (**5c**), 3-Br (**9b**), 3-$SiMe_3$ (**10b**), 4-$SiMe_3$ (**10c**)]

Nitro- and iodo-pentafluorobiphenyls were prepared by electrophilic desilylation of the corresponding trimethylsilyl-containing pentafluorobiphenyls:

$$\begin{tikzcd}
 & \text{3'-(4')}NO_2C_6H_4C_6F_5\ (\mathbf{6b}\text{ or }\mathbf{6c}) \\
\text{3'-(4')-}Me_3SiC_6H_4C_6F_5\ (\mathbf{10b}\text{ or }\mathbf{10c}) \arrow[ur, "HNO_3,\ BF_3"] \arrow[dr, "ICl"'] & \\
 & \text{3'-(4')}IC_6H_4C_6F_5\ (\mathbf{8b}\text{ or }\mathbf{8c})
\end{tikzcd}$$

2,3,4,5,6-Pentafluoro-2′- and 4′-cyanobiphenyls (**7a** and **7c**) were obtained by the Ullmann reaction from C_6F_5Br, IC_6H_4CN and copper powder. 2,3,4,5,6-Pentafluoro-3′-cyanobiphenyl (**7b**) was prepared by the reaction of 2,3,4,5,6-pentafluoro-3′-bromobiphenyl (**9b**) with CuCN in DMF. The identification of 2′-$NO_2C_6H_4C_6F_5$ (**6a**) was performed by using a mixture of 2′-, 3′- and 4′-$NO_2C_6H_4C_6F_5$ isomers (**6a, 6b** and **6c**) produced by nitration of 2,3,4,5,6-pentafluorobiphenyl [20]. It should be noted that the ^{19}F NMR spectrum of 4′-$NO_2C_6H_4C_6F_5$ (**6c**) which we have obtained differs from the one published earlier {−137.8 ppm (F-2,6), −147.8 ppm (F-4), −156.1 ppm (F-3,5) [21]} (cf. Table 4), probably due to the use of C_6F_6 as the external reference by the authors of ref. 21. The syntheses of 2,3,4,5,6-pentafluoro-2′-trifluoromethylbiphenyl (**5a**) and 2,3,4,5,6-pentafluoro-2′-iodo-biphenyl (**8a**) will be described elsewhere. Hexafluorobiphenyls $FC_6H_4C_6F_5$ (**4a, 4b** and **4c**) were identified via their ^{19}F NMR spectra [12, 22].

Experimental

The ^1H and ^{19}F NMR spectra were recorded on a Varian EM 360 L (^1H at 60 MHz and ^{19}F at 56.4 MHz), a Bruker WP 80 SY (^{19}F at 75.4 MHz) and a WP 200 SY (^1H at 200 MHz, ^{19}F at 188.3 MHz) spectrometer (TMS and C_6F_6 as internal references). The chemical shifts $\delta(F)$ were assigned to $CFCl_3$ using a $\delta(F)$ value for C_6F_6 of −162.9 ppm. The IR spectra were recorded on a Specord M 80 instrument in KBr and the high-resolution mass spectra on a Finnigan MAT 8200 spectrometer.

Acetonitrile was refluxed over $KMnO_4$, dried with P_4O_{10} and CaH_2 and stored over 3 Å molecular sieves.

Moisture-sensitive solids were handled in a Braun glovebox MB 100 G. All experiments with $[C_6F_5Xe]^+[AsF_6]^-$ were performed under a dry argon atmosphere in PTFE–FEP tube reactors. Tables 4–6 list the NMR, IR and analytical data for the new compounds.

Reactions of $[C_6F_5Xe]^+[AsF_6]^-$ (2) with aromatic compounds

Acetonitrile (0.10–0.15 ml) was added to a known weight of salt **2**. To the light yellow solution formed, an aromatic compound was added with a syringe. The reaction mixture was kept at room temperature until the $[C_6F_5Xe]^+$ signals disappeared from the ^{19}F NMR spectrum. The yields of products were determined by ^{19}F NMR methods using benzotrifluoride as a quantitative internal reference. The compounds were identified by adding samples prepared independently. The results are given in Table 1.

TABLE 4

Nuclear magnetic resonance spectral data

Compound	Solvent	^1H NMR δ (ppm)	^{19}F NMR δ (ppm)		
			F-2,6	F-4	F-3,5
2'-$CH_3C_6H_4C_6F_5$ (**3a**)	CD_3OD	7.25 (C_6H_4); 1.13 (CH_3)	−140.8	−156.4	−163.1
3'-$CH_3C_6H_4C_6F_5$ (**3b**)	CD_3OD	7.42–7.20 (C_6H_4); 2.40 (CH_3)	−143.0	−157.0	−163.2
4'-$CH_3C_6H_4C_6F_5$ (**3c**)	C_6D_6	7.04 (AA'BB') (C_6H_4); 1.09 (CH_3)	−144.0	−157.0	−163.0
3'-$Me_3SiC_6H_4C_6F_5$ (**10b**)	CD_3OD	7.62–7.38 (C_6H_4); 0.28 ($SiMe_3$)	−143.1	−156.7	−163.1
4'-$Me_3SiC_6H_4C_6F_5$ (**10c**)	CD_3OD	7.52 (AA'BB') (C_6H_4); 0.30 ($SiMe_3$)	−143.0	−156.8	−163.1
3'-$NO_2C_6H_4C_6F_5$ (**6b**)	CD_3OD	7.90–7.50 (C_6H_4)	−143.0	−154.6	−162.3
4'-$NO_2C_6H_4C_6F_5$ (**6c**)	CD_3OD	8.10 (AA'BB') (C_6H_4)	−142.6	−154.4	−162.3
4'-$NO_2C_6H_4C_6F_5$ (**6c**)	$CDCl_3$	8.07 (AA'BB') (C_6H_4)	−143.5	−153.6	−161.9
2'-$CF_3C_6H_4C_6F_5$ (**5a**)[a]	$CDCl_3$		−139.8	−153.1	−163.2
3'-$CF_3C_6H_4C_6F_5$ (**5b**)[b]	CD_3OD	7.85–7.45 (C_6H_4)	−143.3	−155.1	−162.5
4'-$CF_3C_6H_4C_6F_5$ (**5c**)[c]	CD_3OD	7.75 (AA'BB') (C_6H_4)	−142.9	−155.1	−162.6
4'-$CF_3C_6H_4C_6F_5$ (**5c**)	$CDCl_3$		−143.9	−154.9	−162.6
2'-$CNC_6H_4C_6F_5$ (**7a**)	CD_3OD	8.00–7.64 (C_6H_4)	−140.4	−153.2	−162.0
3'-$CNC_6H_4C_6F_5$ (**7b**)	CD_3OD	7.93–7.74 (C_6H_4)	−143.0	−154.9	−162.5
4'-$CNC_6H_4C_6F_5$ (**7c**)	$CDCl_3$	7.66 (AA'BB') (C_6H_4)	−143.8	−154.0	−162.0
3'-$BrC_6H_4C_6F_5$ (**9b**)	CD_3OD	7.69–7.44 (C_6H_4)	−142.9	−155.6	−162.7
3'-$IC_6H_4C_6F_5$ (**8b**)	CD_3OD	7.87–7.29 (C_6H_4)	−142.9	−155.7	−162.7
4'-$IC_6H_4C_6F_5$ (**8c**)	$CD_3OD + C_6D_6$	7.19 (AA'BB') (C_6H_4)	−143.5	−155.8	−162.6
11b[d]	C_6D_6	7.70–6.97 (C_6H_4)	−143.9		−143.9
11c[e]	C_6D_6	7.47 (AA'BB') (C_6H_4)	−144.2		−144.2
1-$C_5H_{11}OC_6F_4H$ (**12**)	CD_3OD	6.99 (C_6F_4H); 4.21 (OCH_2); 1.77–1.39 $(CH_2)_3$; 0.95 (CH_3)	−157.2		−140.3

[a] In $CF_3C_6H_4C_6F_5$ isomer mixture.

[b] $\delta(CF_3)$, −62.5 ppm.

[c] $\delta(CF_3)$, −62.2 ppm.

[d] 1,4-$(3'-CF_3C_6H_4)_2C_6F_4$: $\delta(CF_3)$, −62.6 ppm.

[e] 1,4-$(4'-CF_3C_6H_4)_2C_6F_4$: $\delta(CF_3)$, −63.7 ppm.

TABLE 5

Infrared spectral data

Compound	Wavenumber ($\mathrm{cm^{-1}}$)
$3'$-$\mathrm{Me_3SiC_6H_4C_6F_5}$ (**10b**)	3032; 2956; 2896; 1652; 1522; 1498; 1480; 1388; 1340; 1324; 1252; 1120; 1068; 990; 892; 840; 806; 754; 736; 708; 692; 648; 620.
$4'$-$\mathrm{Me_3SiC_6H_4C_6F_5}$ (**10c**)	3068; 3028; 2956; 2900; 1654; 1600; 1550; 1526; 1504; 1496; 1488; 1392; 1340; 1324; 1252; 1118; 1108; 1062; 990; 842; 828; 736; 700; 624; 516.
$3'$-$\mathrm{NO_2C_6H_4C_6F_5}$ (**6b**)	3100; 2964; 1652; 1544; 1526; 1496; 1434; 1108; 1090; 1074; 990; 920; 904; 836; 812; 744; 724; 700; 680; 644.
$4'$-$\mathrm{NO_2C_6H_4C_6F_5}$ (**6c**)	3104; 1658; 1604; 1524; 1508; 1494; 1404; 1396; 1350; 1312; 1288; 1200; 1108; 1064; 1012; 988; 864; 840; 748; 740; 728; 688; 438.
$3'$-$\mathrm{CF_3C_6H_4C_6F_5}$ (**5b**)[a]	3080; 1654; 1526; 1502; 1490; 1446; 1420; 1388; 1338; 1310; 1284; 1198; 1172; 1134; 1100; 1080; 1068; 990; 908; 896; 812; 780; 768; 700; 676; 664; 644.
$4'$-$\mathrm{CF_3C_6H_4C_6F_5}$ (**5c**)	1656; 1620; 1580; 1534; 1516; 1490; 1432; 1408; 1326; 1178; 1164; 1146; 1126; 1108; 1062; 1020; 988; 956; 860; 848; 768; 720; 600; 508; 404.
$2'$-$\mathrm{CNC_6H_4C_6F_5}$ (**7a**)	3084; 2236; 1654; 1596; 1572; 1526; 1500; 1484; 1448; 1324; 1284; 1188; 1108; 1062; 1032; 990; 968; 864; 800; 774; 716; 644; 556; 492.
$3'$-$\mathrm{CNC_6H_4C_6F_5}$ (**7b**)	3084; 2932; 2236; 1652; 1580; 1528; 1498; 1480; 1436; 1410; 1332; 1232; 1164; 1080; 990; 920; 900; 808; 780; 758; 688; 656; 584.
$4'$-$\mathrm{CNC_6H_4C_6F_5}$ (**7c**)	3000; 2240; 1722; 1654; 1562; 1530; 1510; 1488; 1408; 1280; 1188; 1112; 1076; 1066; 988; 860; 780; 756; 554.
$3'$-$\mathrm{BrC_6H_4C_6F_5}$ (**9b**)	3064; 1654; 1596; 1562; 1522; 1496; 1480; 1432; 1404; 1380; 1320; 1096; 1080; 1064; 988; 912; 892; 879; 804; 770; 736; 698; 684.
$3'$-$\mathrm{IC_6H_4C_6F_5}$ (**8b**)	1652; 1564; 1524; 1496; 1476; 1428; 1396; 1096; 1076; 1062; 988; 912; 876; 800; 764; 736; 688; 680.
$4'$-$\mathrm{IC_6H_4C_6F_5}$ (**8c**)	3060; 1656; 1592; 1560; 1524; 1490; 1392; 1322; 1200; 1068; 1060; 1008; 1000; 986; 944; 852; 828; 806; 772; 500.
1,4-($3'$-$\mathrm{CF_3C_6H_4)_2C_6F_4}$ (**11b**)	3084; 1524; 1496; 1480; 1434; 1408; 1342; 1330; 1320; 1300; 1282; 1186; 1176; 1128; 1096; 1078; 978; 950; 908; 816; 804; 772; 760; 752; 704; 692; 672; 644.
1,4-($4'$-$\mathrm{CF_3C_6H_4)_2C_6F_4}$ (**11c**)	1622; 1472; 1406; 1336; 1320; 1170; 1132; 1108; 1070; 1020; 978; 954; 840; 766; 676; 600.
1-$\mathrm{C_5H_{11}OC_6F_4H}$ (**12**)[a]	3088; 2960; 2935; 2870; 1638; 1514; 1489; 1470; 1400; 1383; 1266; 1215; 1170; 1120; 1087; 966; 937; 871; 822; 733; 707.

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[a] Neat liquid.

TABLE 6

Analytical data

Compound	Found (%) Calculated (%)			Empirical formula
	C	H	F	
3′-$Me_3SiC_6H_4C_6F_5$ (**10b**)	57.2 56.9	4.37 4.11	30.0 30.1	$C_{15}H_{13}F_5Si$
4′-$Me_3SiC_6H_4C_6F_5$ (**10c**)	56.7 56.9	4.32 4.11	29.8 30.1	$C_{15}H_{13}F_5Si$
3′-$NO_2C_6H_4C_6F_5$ (**6b**)[a]	50.5 49.8	1.52 1.38	32.5 32.9	$C_{12}H_4F_5NO_2$
3′-$CF_3C_6H_4C_6F_5$ (**5b**)	50.3 50.0	1.41 1.28	48.6 48.7	$C_{13}H_4F_8$
1,4-(3′-$CF_3C_6H_4)_2C_6F_4$ (**11b**)	55.2 54.8	1.96 1.82	43.6 43.4	$C_{20}H_8F_{10}$
1,4-(4′-$CF_3C_6H_4)_2C_6F_4$ (**11c**)	54.7 54.8	1.96 1.82	43.4 43.4	$C_{20}H_8F_{10}$
1-$C_5H_{11}OC_6F_4H$ (**12**)	55.9 55.9	5.00 5.08	31.9 32.2	$C_{11}H_{12}F_4O$

[a] Found: N, 4.94%; calculated: N, 4.84%.

No reaction occurred on treatment of a suspension of salt **2** in dichloromethane with fluorobenzene or benzotrifluoride for 122 h, or of an acetonitrile solution of salt **2** with the pentafluorobenzene derivatives C_6F_5X (X = H, F, I, CN, $SiMe_3$) (60–70 h).

Fluorination of iodopentafluorobenzene with xenon difluoride in the presence of $BF_3 \cdot OEt_2$

Xenon difluoride (0.199 g, 1.18 mmol) was added gradually to a stirred solution of iodopentafluorobenzene (0.294 g, 1.00 mmol) and $BF_3 \cdot OEt_2$ (20 μl, 0.16 mmol) in 1.5 ml of dichloromethane placed in an FEP reactor. When gas evolution stopped, the mixture was stirred for a further 30 min and the volatile components were removed *in vacuo* to produce 0.291 g (88%) of difluoroiodopentafluorobenzene.

Reaction of $C_6F_5IF_2$ with $B(C_6F_5)_3$

A cool (−50 °C) solution of $B(C_6F_5)_3$ (77.1 mg, 0.15 mmol) in 0.4 ml of MeCN was added to a cool (−50 °C) solution of $C_6F_5IF_2$ (50 mg, 0.15 mmol) in acetonitrile (0.25 ml). After 4 d at −50 °C, all the borane had reacted. According to ^{19}F NMR spectroscopy $[(C_6F_5)_2I]^+X^-$ was formed in quantitative yield {X = BF_4 (37 mol%) and $(C_6F_5)_3BF$ (63 mol%)} In dichloromethane (−50 °C), the reaction was faster (< 1 h) and gave a suspension. The solid when dissolved in MeCN contained a different mixture of anions X^-: X = BF_4, $C_6F_5BF_3$, $(C_6F_5)_2BF_2$ and $(C_6F_5)_3BF$ (6, 45, 37 and 12 mol%).

Preparation of 2,3,4,5,6-pentafluoro-2'-methylbiphenyl (3a)

A solution consisting of 3.42 g (20 mmol) 2-bromotoluene in 5 ml of ether was added to a cool (−25 °C) solution of 23 mmol of BuLi in 14 ml of hexane and 10 ml of ether. The solution was stirred at 10–20 °C for 1 h and added gradually to a solution of 3.72 g (20 mmol) hexafluorobenzene in 45 ml of ether. The mixture was stirred at room temperature for 1 h, then poured into 5% HCl; the organic layer was separated and the aqueous layer extracted with ether. The combined extracts were washed with water and dried over $CaCl_2$. The solvent was distilled off. The residue was distilled *in vacuo* to give 3.75 g (70%) of the product **3a**, b.p. 78–80 °C/6 mmHg (200–203 °C [11]). The IR spectrum was correct [23].

Preparation of 2,3,4,5,6-pentafluoro-3'-methylbiphenyl (3b)

This was obtained in a similar manner from 4.28 g (25 mmol) 3-bromotoluene, 30 ml of 1.1 M BuLi in pentane and 9 g (48 mmol) hexafluorobenzene in 55 ml of ether. Vacuum distillation gave 4.20 g (65%) of the product **3b**, b.p. 83–85 °C/2 mmHg (236–238 °C [11]). The IR spectrum was correct [23].

Preparation of 2,3,4,5,6-pentafluoro-4'-methylbiphenyl (3c)

This was obtained in a similar manner from 4.28 g (25 mmol) 4-bromotoluene, 30 ml of 1.6 M BuLi in hexane and 4.65 g (25 mmol) hexafluorobenzene in 55 ml of ether. Crystallization from hexane gave 4.06 g (63%) of the product **3c**, m.p. 116–118 °C (117–118 °C [24], 119–120 °C [11]). The IR spectrum was correct [23].

Preparation of 2,3,4,5,6-pentafluoro-3'-bromobiphenyl (9b) (nc)

This compound was prepared similarly from 4.7 g (20 mmol) 1,3-dibromobenzene, 31 ml of 1.1 M BuLi in pentane and 9 g (48 mmol) hexafluorobenzene in 61 mg of ether. Crystallization from MeOH gave 2.9 g (48%) of the product **9b**, m.p. 60–61 °C. Analysis: Found: M^+ 321.9413 (by mass spectrum). $C_{12}H_4BrF_5$ requires: M^+ 321.9417.

Preparation of 2,3,4,5,6-pentafluoro-3'-trifluoromethylbiphenyl (5b) (nc)

This was obtained in a similar manner from 3.38 g (15 mmol) 3-bromobenzotrifluoride, 13 ml of 1.6 M BuLi in hexane and 2.80 g (15 mmol) hexafluorobenzene in 40 ml of ether. After the solvent had been distilled off and the residue crystallized from hexane, 0.74 g (11%) 1,4-bis(3'-trifluoromethylphenyl)tetrafluorobenzene (**11b**) (nc) was isolated, m.p. 126–128 °C. From the mother liquor, 2,3,4,5,6-pentafluoro-3'-trifluoromethylbiphenyl (**5b**) was isolated by preparative GLC methods, b.p. 85–87 °C/14 mmHg.

Preparation of 2,3,4,5,6-pentafluoro-4'-trifluoromethylbiphenyl (5c) (nc)

This was obtained in a similar manner from 3.38 g (15 mmol) 4-bromobenzotrifluoride, 13 ml of 1.6 M BuLi in hexane and 2.80 g (15 mmol) hexafluorobenzene in 50 ml of ether. After the solvent had been distilled off, the residue was crystallized from hexane to give 1.3 g (20%) of 1,4-bis(4′-trifluoromethylphenyl)tetrafluorobenzene (nc) (**11c**), m.p. 228–230 °C. The mother liquor was evaporated and the residue sublimed to give 0.93 g (20%) of 2,3,4,5,6-pentafluoro-4′-trifluoromethylbiphenyl (**5c**), m.p. 59–60 °C (from MeOH). Analysis: Found: M^+ 312.0185 (by mass spectrum). $C_{13}H_4F_8$ requires: M^+ 312.0185.

*Preparation of 2,3,4,5,6-pentafluoro-3′-trimethylsilylbiphenyl (**10b**) (nc)*

This was obtained in a similar manner from 7.43 g (32 mmol) 3-bromophenyltrimethylsilane, 22 ml of 1.6 M BuLi in hexane and 7.0 g (37 mmol) hexafluorobenzene in 55 ml of ether. Vacuum distillation gave 5.20 g (51%) of the product **10b**, b.p. 105–107 °C/8 mmHg.

*Preparation of 2,3,4,5,6-pentafluoro-4′-trimethylsilylbiphenyl (**10c**) (nc)*

This was obtained by a similar procedure from 5.47 g (24 mmol) 4-bromophenyltrimethylsilane, 15 ml of 1.6 M BuLi in hexane and 4.3 g (24 mmol) hexafluorobenzene in 60 ml of ether. Vacuum distillation gave 3.94 g (54%) of the product **10c**, b.p. 111–113 °C/6 mmHg.

*Preparation of 2,3,4,5,6-pentafluoro-3′-iodobiphenyl (**8b**) (nc)*

Iodine monochloride (0.7 g, 4.3 mmol) dissolved in 1 ml of $CHCl_3$ (0 °C) was added dropwise to a solution consisting of 0.52 g (1.57 mmol) 2,3,4,5,6-pentafluoro-3′-trimethylsilylbiphenyl (**10b**) in 1 ml of $CHCl_3$. The solution was stirred for 3 h at room temperature, then treated with an aqueous $Na_2S_2O_5$ solution. The solvent was distilled off and the residue crystallized from MeOH. This gave 0.42 g (72%) of the product **8b**, m.p. 48–49 °C. Analysis: Found: M^+ 369.9291 (by mass spectrum). $C_{12}H_4F_5I$ requires: M^+ 369.9280.

*Preparation of 2,3,4,5,6-pentafluoro-4′-iodobiphenyl (**8c**) (nc)*

This was obtained in a similar manner from 1.58 g (5 mmol) 2,3,4,5,6-pentafluoro-4′-trimethylsilylbiphenyl (**10c**) in 12 ml of CH_2Cl_2 and 0.98 g (6 mmol) ICl in 8 ml of CH_2Cl_2 (0 °C). Yield of product **8c**, 1.21 g (65%), m.p. 110–111 °C. Analysis: Found: M^+ 369.9264 (by mass spectrum). $C_{12}H_4F_5I$ requires: M^+ 369.9280.

*Preparation of 2,3,4,5,6-pentafluoro-3′-nitrobiphenyl (**6b**)*

A solution consisting of 0.35 g (5.6 mmol) 100% HNO_3 and 0.63 g (5.8 mmol) $BF_3 \cdot NCMe$ in 10 ml of MeCN was added to a solution consisting of 0.8 g (2.53 mmol) 2,3,4,5,6-pentafluoro-3′-trimethylsilylbiphenyl (**10b**) in 5 ml of MeCN. The mixture was refluxed for 5 h, then poured on to ice, extracted with dichloromethane and dried over $CaCl_2$. The solvent was distilled off and the residue sublimed to give 0.35 g (48%) of the product **6b**, m.p. 110–112 °C (106–108 °C [22], 113–114 °C [20]).

*Preparation of 2,3,4,5,6-pentafluoro-4'-nitrobiphenyl (**6c**)*

This was obtained similarly from 0.45 g (7.0 mmol) 100% HNO_3, 0.66 g (6.1 mmol) $BF_3 \cdot NCMe$ and 1.36 g (4.3 mmol) 2,3,4,5,6-pentafluoro-4'-trimethylsilylbiphenyl (**10c**) in 10 ml of MeCN. This gave 0.82 g (66%) of the product **6c**, m.p. 89–90 °C (87–89 °C [22], 92–93 °C [20], 93–94 °C [21]). Analysis: Found: M^+ 289.0166 (by mass spectrum). $C_{12}H_4F_5NO_2$ requires: M^+ 289.0162.

*Preparation of 2,3,4,5,6-pentafluoro-2'-cyanobiphenyl (**7a**) (nc)*

Bromopentafluorobenzene (1.1 g, 4.4 mmol), 2-iodobenzonitrile (1.0 g, 4.4 mmol) and copper powder (2.0 g, 31 mmol) were heated in a sealed glass tube for 18 h at 190–200 °C. The mixture was cooled, extracted with hot $CHCl_3$ and the solvent distilled off. The dark residue was extracted with hot hexane and the solvent again distilled off. Preparative TLC (silica gel, eluent CCl_4) gave 0.23 g (31%) decafluorobiphenyl, 0.1 g (22%) 2,2'-dicyanobiphenyl (both compounds identified by IR spectroscopy) and 0.50 g (42%) 2,3,4,5,6-pentafluoro-2'-cyanobiphenyl (**7a**), m.p. 73–74 °C (from pentane). Analysis: Found: M^+ 269.0264 (by mass spectrum). $C_{13}H_4F_5N$ requires: M^+ 269.0264.

*Preparation of 2,3,4,5,6-pentafluoro-4'-cyanobiphenyl (**7c**) (nc)*

This was obtained in a similar manner from bromopentafluorobenzene (1.1 g, 4.4 mmol), 4-iodobenzonitrile (1.0 g, 4.4 mmol) and copper powder (2.0 g, 31 mmol). Yield, 0.32 g (27%) **7c**, m.p. 112–113 °C (from MeOH). Analysis: Found: M^+ 269.0270 (by mass spectrum). $C_{13}H_4F_5N$ requires: M^+ 269.0264.

*Preparation of 2,3,4,5,6-pentafluoro-3'-cyanobiphenyl (**7b**) (nc)*

2,3,4,5,6-Pentafluoro-3'-bromobiphenyl (**9b**) (1.0 g, 3.1 mmol) and CuCN (0.38 g, 4.2 mmol) were refluxed in DMF (3 ml) for 8 h. Then a solution consisting of 0.7 g $FeCl_3 \cdot 6H_2O$ in 7 ml of 1 N HCl was added. The mixture was refluxed for a further 30 min and stream distilled. Yield of product **7b**, 0.65 g (78%), m.p. 75–76 °C (from MeOH). Analysis: Found: M^+ 269.0267 (by mass spectrum). $C_{13}H_4F_5N$ requires: M^+ 269.0264.

Reaction of $C_6F_5NH_2$ and $C_5H_{11}ONO$ with C_6H_5I

Pentyl nitrite (2.5 ml, 19 mmol) was added dropwise to a stirred solution of $C_6F_5NH_2$ (3.0 g, 16 mmol) in iodobenzene (14.9 g, 73 mmol). After a few moments, a vigorous reaction started and the temperature of the reaction mixture spontaneously increased up to 80 °C. After 30 min, the solution was cooled and analyzed by ^{19}F NMR spectroscopy. Yields of compounds C_6F_5I, C_6F_5H, $C_6F_5C_6H_5$, 2'-$IC_6H_4C_6F_5$ (**8a**), 3'-$IC_6H_4C_6F_5$ (**8b**) and 4'-$IC_6H_4C_6F_5$ (**8c**) were 35.8, 8.4, 6.3, 11.5, 7.7 and 12.3%, respectively.

Reaction of $C_6F_5NH_2$ and $C_5H_{11}ONO$ with $C_6H_5SiMe_3$

The reaction of $C_6F_5NH_2$ (0.93 g, 5.2 mmol), pentyl nitrite (1.0 ml, 7.5 mmol) with trimethylsilylbenzene (2.9 g, 19.2 mmol) was conducted at 80

°C as described above (mixing of the reagents was not accompanied by any pronounced exothermal effect). The pentafluorobenzene and 2,3,4,5,6-pentafluorobiphenyl obtained were identified by ^{19}F NMR spectroscopy (yields, 32 and 39%, respectively).

Reaction of $C_6F_5NH_2$ and $C_5H_{11}ONO$ with C_6H_5CN

Pentyl nitrite (1.6 ml, 14 mmol) was added to a solution of $C_6F_5NH_2$ (2.0 g, 11 mmol) in benzonitrile (10 ml, 97 mmol) (80 °C). A mixture of 2′-, 3′- and 4′-$CNC_6H_4C_6F_5$ (**7a, 7b** and **7c**) (yields, 20.4, 24.5 and 13.1%, respectively) resulted. The reaction mixture also contained pentafluorobenzene (yield, 18%) and some unidentified products resulting from the partial oxidation of pentafluoroaniline.

Reaction of $C_6F_5NH_2$ and $C_5H_{11}ONO$ with $C_6H_5CF_3$

A similar reaction between 7.0 g (38 mmol) $C_6F_5NH_2$, 5 ml (43 mmol) of pentyl nitrite with 20 ml (164 mmol) of benzotrifluoride gave a mixture of 2′-, 3′- and 4′-$CF_3C_6H_4C_6F_5$ (**5a, 5b** and **5c**) (yields, 12.1, 31.0 and 12.1%, respectively) and 1-pentyloxy-2,3,5,6-tetrafluorobenzene (29%).

*Preparation of 1-pentyloxy-2,3,5,6-tetrafluorobenzene (**12**) (nc)*

BuLi in pentane (30 ml of a 1.1 M solution) was added via a syringe to 10 ml of pentanol. To the resulting suspension, 5.1 g (30 mmol) pentafluorobenzene were added with stirring. The mixture was heated at 60–70 °C for 6 h, then poured into 5% HCl. The organic layer was separated, diluted with $CHCl_3$ (10 ml), dried over $CaCl_2$ and distilled *in vacuo* to give 2.5 g (35%) of product **12**, b.p. 67–70 °C/7 mmHg.

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