Polyfluoroorganoboron-Oxygen Compounds. 1

Polyfluorinated Aryl(dihydroxy)boranes and Tri(aryl)boroxins

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Received February 11th, 2002; revised May 30th, 2002.

Dedicated to Professor Dietrich Döpp on the Occasion of his 65th Birthday

Abstract. A general preparative procedure for polyfluorinated aryl(dihydroxy)boranes $C_6H_{5-n}F_nB(OH)_2$ (n = 3 − 5) is described. Polyfluorinated aryl(dihydroxy)boranes are easily dehydrated to the corresponding tri(aryl)boroxins $(C_6H_{5-n}F_nBO)_3$ by thermal or chemical treatment. The property of the acids $C_6H_{5-n}F_nB(OH)_2$ to condensate depends on the number and on the position of the fluorine atoms in the aryl group. Examples of both classes of boron compounds were isolated as pure individuals and characterized by multinuclear NMR spectroscopy.

Keywords: Polyfluoroaryl(dihydroxy)boranes (Polyfluorophenylboronic acids); Tris(polyfluoroaryl)boroxins; Dehydration; NMR spectroscopy

Polyfluororganische Bor-Sauerstoff Verbindungen. 1

Polyfluorierte Aryl(dihydroxy)borane und Tri(aryl)boroxine

Inhaltsübersicht. Es wird ein allgemeiner Weg für die Darstellung polyfluorierter Aryl(dihydroxy)borane beschrieben. Polyfluorierte Aryl(dihydroxy)borane lassen sich thermisch und chemisch leicht dehydratisieren und gehen dabei in die entsprechenden Tri(aryl)boroxine über. Die Neigung zur Kondensation hängt sowohl von der Anzahl als auch von der Stellung der Fluoratome in der Arylgruppe ab. Es werden Beispiele für beide Klassen von Borverbindungen vorgestellt, die in Reinsubstanz isoliert und durch Multikern-NMR-Spektroskopie charakterisiert wurden.

Introduction

Aryl(dihydroxy)boranes (often named arylboronic acids) are well-known compounds which are widely used in organic synthesis [1, 2]. However, polyfluorinated derivatives $C_6H_{5-n}F_nB(OH)_2$ (n ≥ 3) and, especially their anhydrides, tri(aryl)boroxins, have been less investigated. 3,4,5-Trifluorophenyl(dihydroxy)borane which had been prepared by nucleophilic arylation of $B(OMe)_3$ with 3,4,5-$C_6H_2F_3MgBr$ in THF and subsequent hydrolysis of the reaction mixture in 58 % yield, was characterized by ^{1}H NMR and IR spectroscopy as a mixture (14 : 86) of the acid and the corresponding tri(aryl)boroxin [3, 4]. The mixture was used as a catalyst for the direct amidation of aliphatic carboxylic acids [3] and was employed in the *Suzuki* reaction with aryl iodides [5]. 2,4,6-Trifluorophenyl- and 2,3,4,5-tetrafluorophenyl(dihydroxy)boranes were mentioned as reactants but their preparation and characteristic properties were not reported [3, 6]. Pentafluorophenyl(dihydroxy)borane was obtained by *Chambers* and *Chivers* by hydrolysis of pentafluorophenyldichloroborane in aqueous acetone at −78 °C in 89 % yield [7] and underwent slow hydrodeboration in aqueous solution (20 % conversion at 20 °C, 2 days) and formed pentafluorophenol in the reaction with 85 % H_2O_2 [7].

Tris(pentafluorophenyl)boroxin was obtained by crystallisation of crude $C_6F_5B(OH)_2$ from toluene, by the thermolysis of 2-pentafluorophenyl-1,3,2-dioxaborolandione-4,5 at 110 − 130 °C [8] or by the reaction (−30 °C, 24 h) of $C_6F_5B{=}NC(CH_3)_3$ with benzophenone as reported by *Paetzold* [9].

The goal of our study was a general synthetic approach to polyfluorophenyl(dihydroxy)boranes $C_6H_{5-n}F_nB(OH)_2$ (n ≥ 3), their adequate characterization and the preparation and characterization of the corresponding tri(aryl)boroxins. The main problem with polyfluorophenyl(dihydroxy)boranes arises from the ease of dehydration of aryl(dihydroxy)boranes, even under mild conditions [2] which often leads to mixtures of the acids and their anhydrides instead of the

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pure acids. E.g., the fluorinated arylboronic acids [aryl(dihydroxy)boranes] offered commercially are advertised with the melting points of their anhydrides [10].

Results and Discussion

The syntheses of fluoro-containing phenyl(dihydroxy)boranes were carried out by reacting arylmagnesium bromides or aryllithium nucleophiles with a slight excess of $B(OMe)_3$ in ether and subsequent hydrolysis of the aryltrimethoxyborates [11, 12] formed as intermediates with diluted HCl.

$$\mathrm{MAr} \xrightarrow{\mathrm{B(OMe)_3,\ ether}} \mathrm{M\,[ArB(OMe)_3]} \xrightarrow{\mathrm{aq.\ HCl}} \underset{\mathbf{1-9}}{\mathrm{ArB(OH)_2}}$$

M = MgBr, Li
Ar = C_6F_5 (**1**), 2,3,4,5-C_6HF_4 (**2**), 2,3,4,6-C_6HF_4 (**3**), 2,3,5,6-C_6HF_4 (**4**), 2,4,6-$C_6H_2F_3$ (**5**), 3,4,5-$C_6H_2F_3$ (**6**), 2,6-$C_6H_3F_2$ (**7**), 2,4-$C_6H_3F_2$ (**8**), and 4-C_6H_4F (**9**),

Although it is generally known that aryl(dihydroxy)boranes eliminate water readily [1, 2], the acids **1** − **5**, and **7** could be crystallized from boiling toluene without dehydration. However, the acids **6** and **9** without any fluorine atom in *ortho* position, as well as **8** eliminated water during the crystallisation from boiling toluene and formed the corresponding tri(aryl)boroxins **6a**, **9a** and **8a**, respectively.

$$3\ \mathrm{ArB(OH)_2} \xrightarrow[-\,3\ \mathrm{H_2O}]{\mathrm{toluene,\ reflux}} \underset{\mathbf{6a,\ 8a,\ 9a}}{\mathrm{(ArBO)_3}}$$

Ar = 3,4,5-$C_6H_2F_3$ (**6**), 2,4-$C_6H_3F_2$ (**8**), 4-C_6H_4F (**9**)

The intended conversion of polyfluorinated aryl(dihydroxy)boranes into the corresponding tri(aryl)boroxins was achieved either by thermal or by chemical dehydration. E.g., heating of acid **1** and **4** at 100 °C for 2 − 2.5 h over P_4O_{10} resulted in the quantitative formation of boroxin **1a** and **4a**, respectively.

$$3\ \mathrm{(4\text{-}XC_6F_4B(OH)_2} \xrightarrow[-\,3\ \mathrm{H_2O}]{\mathrm{P_4O_{10},\ 100-110\ ^\circ C}} \underset{\mathrm{X = F\ (\mathbf{1a}),\ H\ (\mathbf{4a})}}{\mathrm{(4\text{-}XC_6F_4BO)_3}}$$

Alternatively, the fast and quantitative conversion of acids **1**, **4** and **6** into the boroxins **1a**, **4a** and **6a** occurred in ethereal solution, using thionyl chloride at room temperature.

$$3\ \mathrm{ArB(OH)_2} + 3\ \mathrm{SOCl_2} \xrightarrow{\mathrm{ether,\ 20\ ^\circ C}} \mathrm{(ArBO)_3} + 3\ \mathrm{SO_2} + 6\ \mathrm{HCl}$$

Ar = C_6F_5 (**1a**), 2,3,5,6-C_6HF_4 (**4a**), 3,4,5-$C_6H_2F_3$ (**6a**)

The successful preparation of the polyfluorinated aryl(dihydroxy)boranes **1** − **8**, as well as of the polyfluorinated tri(aryl)boroxins **1a**, **4a**, **6a**, **8a**, and **9a** enabled to study some of their individual properties.

The polyfluoroaryl(dihydroxy)boranes **1** − **9** are readily soluble in acetone, acetonitrile, ether and moderately soluble in dichloromethane and toluene. As a general rule, the solubility of the tris(polyfluoroaryl)boroxins is significantly less than that of the corresponding aryl(dihydroxy)boranes. For instance, the addition of sub-stoichiometric amounts of $SOCl_2$ to the solution of $C_6F_5B(OH)_2$ or 3,4,5-$C_6H_2F_3B(OH)_2$ in ether immediately caused precipitation of the boroxins $(C_6F_5BO)_3$ or (3,4,5-$C_6H_2F_3BO)_3$, whereas the unreacted aryl(dihydroxy)boranes remained still in solution. Alternatively, a suspension of $(ArBO)_3$ in ether or MeCN was easily converted into the solution of the acid $ArB(OH)_2$ by the addition of stoichiometric amounts of water.

$$3\ \mathrm{ArB(OH)_2} \underset{\mathrm{ether,\ +\ H_2O}}{\overset{\mathrm{ether,\ +\ SOCl_2}}{\rightleftharpoons}} \mathrm{(ArBO)_3}\downarrow$$

Ar = C_6F_5, 2,3,5,6-C_6HF_4, 3,4,5-$C_6H_2F_3$, 2,4-$C_6H_3F_2$, 4-C_6H_4F

The visually monitored thermal decomposition of the fluoroaryl(dihydroxy)boranes **1** − **9** obviously demonstrates the complex nature of the thermal processes above 80 − 90 °C, e.g., sublimation, phase transformation and dehydration, ending with the formation of the high melting (> 200 °C) solid boroxins. Differential scanning calorimetry (DSC) confirmed this complex picture of endothermal conversions of acids **1** − **9** when heated between 100 and 300 °C. We consider, that no defined melting points can be attributed to the fluorinated aryl(dihydroxy)boranes **1** − **9** under normal conditions with certainty because of the different processes mentioned above. Whereas well defined melting points were observed for tri(aryl)boroxins visually, as well as by DSC.

Tris(pentafluorophenyl)boroxin (**1a**), e.g., showed only one endothermic effect at 284 °C (DSC: reversible, melting point), comparable to the observed melting point of 282 °C [8] for **1a**. The melting point of 290 °C reported for the product obtained by sublimation of pentafluorophenyl(dihydroxy)borane at 140 °C (0.01 mm Hg [7]) which was attributed to acid **1** is not correct. The tri(aryl)boroxins **4a** and **6a** melted at 214 °C and 292 °C, and the anhydrides **8a** and **9a** melted at 248 °C and 263 °C. The melting points reported for the corresponding acids **8** and **9** of 247 − 250 and 263 − 265 °C are not correct [10], because they refer to the thermal behaviour of the anhydrides.

The polyfluorinated aryl(dihydroxy)boranes **1** − **9** and the tri(aryl)boroxins **1a**, **4a**, **6a**, **8a**, and **9a** were characterized by multinuclear NMR spectroscopy in solution (Tables 1 − 4).

The ^{11}B NMR spectra of the polyfluorophenyl(dihydroxy)boranes **1** − **9** in acetone-d_6 or in ether displayed broad resonances ($\tau_{1/2}$ 90 − 195 Hz) in the narrow range from 26 to 28 ppm (Table 3). This region is common for aryl(dihy-

Table 1 The ^1H NMR spectra of polyfluorinated aryl(dihydroxy)boranes $ArB(OH)_2$ and tri(aryl)boroxins $(ArBO)_3$

Aryl group		Solvent	Chemical shifts, ppm						Coupling constants, Hz
			O−H	H^2	H^3	H^4	H^5	H^6	
C_6F_5	**1**	acetone-d_6	8.19						
2,3,4,5-C_6HF_4	**2**	acetone-d_6 a)	b)					7.34	(H^6,F^2) 4.7, (H^6,F^3) 2.7, (H^6,F^4) 8.9, (H^6,F^5) 10.5
2,3,4,6-C_6HF_4	**3**	acetone-d_6 a)	b)				7.04		(H^5,F^3) 5.3, (H^5,F^4) 10.6, (H^5,F^6) 8.6, (H^5,F^2) 2.5
2,3,5,6-C_6HF_4	**4**	acetone-d_6	8.15			7.44			(H^4,F^2) 7.6, (H^4,F^3) 10.1
2,3,5,6-C_6HF_4	**4**	ether c)	7.53			7.11			(H^4,F^2) 7.4, (H^4,F^3) 9.8
2,3,5,6-C_6HF_4	**4a**	ether c)				6.74			unresolved complex multiplet
2,4,6-$C_6H_2F_3$	**5**	acetone-d_6	7.79		6.82		6.82		(H^3,F^2) 9.4, (H^3,F^4) 7.4
3,4,5-$C_6H_2F_3$	**6**	acetone-d_6 a)	b)	7.53				7.53	(H^2,F^3) 8.7, (H^2,F^4) 7.4
3,4,5-$C_6H_2F_3$	**6**	ether c)	6.95	7.38				7.38	(H^2,F^3) 8.4, (H^2,F^4) 7.5
3,4,5-$C_6H_2F_3$	**6a**	ether c)		7.67				7.67	$(H^2,F^3) \approx (H^2,F^4) \approx 7.4$
3,4,5-$C_6H_2F_3$ [3]	**6**	$CDCl_3$ c)	4.74−4.82	7.35				7.35	t, 7.0 d
3,4,5-$C_6H_2F_3$ [3]	**6a**	$CDCl_3$ c)		7.77				7.77	t, 7.9 d
2,6-$C_6H_3F_2$	**7**	acetone-d_6	7.74		6.90	7.40	6.90		(H^3,F^2) 10.3, (H^4,F^2) 6.5
2,4-$C_6H_3F_2$	**8**	acetone-d_6 a)	b)		6.90		6.98	7.78	(H^3,F^2) 9.7, (H^3,F^4) 9.7, (H^5,F^4) 8.5, (H^5,H^6) 8.4, (H^6,F^2) 7.5, (H^6,F^4) 7.5
4-C_6H_4F	**9**	acetone-d_6 a)	b)	7.89	7.06		7.06	7.89	(H^2,H^3) 8.6, (H^2,F^4) 6.4, (H^3,F^4) 9.5

a) Recorded in the presence of D_2O (3 equivalents).
b) H-D exchange.
c) Recorded at 32 °C.
d) Apparent coupling constants.

Table 2 The ^{19}F NMR spectra of fluorinated phenyl(dihydroxy)boranes $ArB(OH)_2$ and tri(aryl)boroxins $(ArBO)_3$

Aryl group		Solvent	Chemical shifts, ppm					Coupling constants, Hz
			F-2	F−3	F−4	F−5	F−6	
C_6F_5	**1**	acetone-d_6	−132.61	−163.50	−154.72	−163.50	−132.61	(F^2,F^6) 10.3, (F^3,F^2) 22.8, (F^3,F^5) 9.4, (F^4,F^3) 19.5
C_6F_5 [7]	**1**	acetone b)	−132.9	−164.1	−155.4	−164.1	−132.9	not reported
C_6F_5	**1**	ether b)	−132.13	−163.35	−155.09	−163.35	−132.13	not determined
C_6F_5	**1**	CH_2Cl_2	−133.31	−162.06	−150.03	−162.06	−133.31	(F^4,F^3) 20.1, (F^4,F^2) 4.6
C_6F_5	**1**	CH_3CO_2H b)	−131.86	−162.72	−153.17	−162.72	−131.86	(F^2,F^6) 8.5, (F^3,F^2) 22.0, (F^3,F^5) 10.0, (F^4,F^2) 3.0, (F^4,F^3) 19.0
C_6F_5	**1a**	ether b)	−132.37	−163.66	−154.07	−163.66	−132.37	unresolved resonances
2,3,4,5-C_6HF_4	**2**	acetone-d_6 a)	−131.69	−158.17	−155.27	−141.14		(F^2, F^3) 21.2, (F^2,F^4) 5.0, (F^2,F^5) 15.1, (F^2,H^6) 4.7, (F^3,F^4) 18.8, (F^3,F^5) 2.2, (F^3,H^6) 2.7, (F^4,F^5) 20.2, (F^4,H^6) 8.9, (F^5,H^6) 10.5
2,3,5,6-C_6HF_4	**4**	acetone-d_6	−133.70	−140.34		−140.34	−133.70	(F^2,F^3) 22.7, (F^2,H^4) 7.6, (F^2,F^5) 15.1, (F^3,H^4) 10.1
2,3,5,6-C_6HF_4	**4**	ether b)	−133.28	−140.27		−140.27	−133.28	not determined
2,3,5,6-C_6HF_4	**4a**	ether b)	−131.60	−139.94		−139.94	−131.60	unresolved resonances
2,3,4,6-C_6HF_4	**3**	acetone-d_6 a)	−126.22	−168.26	−132.81		−106.12	(F^2,F^3) 21.7, (F^2,F^4) 6.9, (F^3,F^4) 20.5, (F^3,H^5) 5.3, (F^3,F^6) 11.7, (F^4,H^5) 10.6, (F^6,H^5) 8.63, (F^4,F^6) 3.3
2,3,4,6-C_6HF_4	**3**	acetonitrile-d_3 b)	−125.56	−167.16	−131.51		−105.80	(F^2,F^3) 21, (F^2,F^4) 7, (F^3,F^4) 20, (F^3,H^5) 6, (F^3,F^6) 12, (F^4,H^5) 10, (F^4,F^6) 4, (F^6,H^5) 10
2,4,6-$C_6H_2F_3$	**5**	acetone-d_6	−99.95		−107.67		−99.95	(F^2,H^3) 7.4, (F^2,F^4) 7.6, (F^4,H^3) 9.4
3,4,5-$C_6H_2F_3$	**6**	acetone-d_6 a)		−136.41	−159.65	−136.41		(F^3,H^2) 8.7, (F^4,H^2) 7.3, (F^3,F^4) 19.5
3,4,5-$C_6H_2F_3$	**6**	ether b)		−136.41	−159.51	−136.41		not determined
3,4,5-$C_6H_2F_3$	**6a**	ether b)		−135.52	−156.50	−135.52		unresolved resonances
2,6-$C_6H_3F_2$	**7**	acetone-d_6	−103.16				−103.16	(F^2,H^3) 10.3, (F^2H^4) 6.5
2,4-$C_6H_3F_2$	**8**	acetone-d_6 a)	−101.37		−107.65			(F^2,H^3) 9.7, (F^2,F^4) 9.8, (F^2,H^6) 7.5, (F^4,H^3) 9.7, (F^4,H^5) 8.5, (F^4,H^6) 7.4
2,4-$C_6H_3F_2$	**8**	CH_2Cl_2/CD_2Cl_2	−105.97		−105.72			
4-C_6H_4F	**9**	acetone-d_6 a)			−110.98			(F^4,H^2) 6.4, (F^4,H^3) 9.5
4-C_6H_4F	**9**	ether b)			−111.52			not determined
4-C_6H_4F	**9a**	ether b)			−106.34			not determined

a) Recorded in the presence of D_2O (3 equivalents).
b) Recorded at 32 °C.

droxy)boranes in basic solvents [13]. The comparison of the chemical shifts of highly fluorinated ($n \geq 3$) acids with those of the less fluorinated ($n = 1, 2$) acids $C_6H_{5-n}F_nB(OH)_2$ demonstrates the independence of ^{11}B shift values of the number and the position of fluorine atoms bonded to the aromatic ring (Table 3). A similar narrow range, but more to low frequency is observed in the ^{11}B NMR spectra of the penta- and tetrafluorophenylboroxins (**1a**) and (**4a**), and of the difluorophenylboroxins (**7a**) and (**8a**). These boroxins have in common at least one fluorine atom in *ortho*-position to boron. Their ^{11}B signals at 18 − 19 ppm are broader than those of the corresponding acids. However, the ^{11}B chemical shifts of boroxins (3,4,5-$C_6H_2F_3BO)_3$ and (4-$C_6H_4FBO)_3$ (without any fluorine

Table 3 The ^{11}B NMR spectra of fluorinated phenyl(dihydroxy)boranes $ArB(OH)_2$ and tri(aryl)boroxins $(ArBO)_3$

Aryl group		Solvent	Chemical shift, ppm	$\tau_{1/2}$, Hz
C_6F_5	**1**	acetone-d_6	26.93	112
C_6F_5	**1**	ether	26.21	98
C_6F_5	**1a**	ether	18.58	255
C_6F_5 [13]	**1a**	toluene-d_7	20.1	not reported
2,3,4,5-C_6HF_4	**2**	acetone-d_6 [a]	27.08	165
2,3,4,6-C_6HF_4	**3**	acetone-d_6 [a]	27.24	116
2,3,5,6-C_6HF_4	**4**	acetone-d_6	27.21	124
2,3,5,6-C_6HF_4	**4**	ether	26.61	105
2,3,5,6-C_6HF_4	**4a**	ether	19.51	142
2,4,6-$C_6H_2F_3$	**5**	acetone-d_6	27.76	119
3,4,5-$C_6H_2F_3$	**6**	acetone-d_6 [a]	27.59	161
3,4,5-$C_6H_2F_3$	**6**	ether	27.18	97
3,4,5-$C_6H_2F_3$	**6a**	ether	27.18	97
2,6-$C_6H_3F_2$	**7**	acetone-d_6	28.06	105
2,6-$C_6H_3F_2$	**7**	ether	27.37	67
2,6-$C_6H_3F_2$	**7a**	ether	19.02	96
2,4-$C_6H_3F_2$	**8**	acetone-d_6 [a]	28.01	136
2,4-$C_6H_3F_2$	**8**	ether	27.36	86
2,4-$C_6H_3F_2$	**8**	CH_2Cl_2/CD_2Cl_2	27.96	74
2,4-$C_6H_3F_2$	**8a**	ether	19.10	104
4-C_6H_4F	**9**	acetone-d_6 [a]	28.53	195
4-C_6H_4F [13]	**9**	$CDCl_3$	27.5	not reported
4-C_6H_4F	**9**	ether	28.08	141
4-C_6H_4F	**9a**	ether	28.08	141
C_6H_5 [13]	**10**	EtOH	28.4	not reported
σC_6H_5 [13]	**10a**	CS_2	30.4	not reported

[a] Recorded in the presence of D_2O (3 equivalents).

atom in the *ortho*-positions) coincide practically with the chemical shifts of the corresponding acids **6** and **9**, respectively. A specially prepared solution of approximately equal amounts of the corresponding compounds **6/6a** and **9/9a** showed separate resonances for the aryl(dihydroxy)borane and the corresponding tri(aryl)boroxin in the ^{1}H and ^{19}F NMR spectra but only one signal in the ^{11}B NMR spectra [*cf.* literature data for $C_6H_5B(OH)_2$ and $(C_6H_5BO)_3$, Table 3].

In the case of acid **1** we have investigated the influence of solvents on the ^{19}F shift values. We compared the three resonances of the C_6F_5 group in the oxygen-basic solvents acetone and ether with those in the non-basic polar solvent CH_2Cl_2 and in the protic acid CH_3CO_2H. The significantly low frequency shifts of the *p*- and the *m*-F atoms in the oxygen-basic solvents are in agreement with a weak base coordinating at boron or a polarisation of the O-H bond by the basic solvent.

The ^{13}C NMR spectra of fluorinated phenyl(dihydroxy)boranes in acetone solutions are presented in Table 4. The signals of the carbon atom C-1 of pentafluorophenyl-, 2,3,4,6-tetrafluorophenyl- and 2,4,6-trifluorophenyl(dihydroxy)boranes with fluorine atoms in *para*- and both *ortho*-positions to boron are located in the narrow range from 109 to 111 ppm. Replacement of the fluorine atom by hydrogen in *para*-position (acid **4**) and especially, in the *ortho*-position(s) (acids **2** and **6**) caused a significant deshielding of the C-1 signal. The influence of fluorine atoms in *ortho* position(s) to boron is well demonstrated by the ^{13}C NMR spectra in the series of isomeric tetrafluorophenyl-, trifluorophenyl- and difluorophenyl(dihydroxy)boranes (Table 4). In addition, the comparison of the ^1J(C,F) coupling constants for acids **1** − **9** shows that fluorine atoms in *ortho* positions to boron give rise to the smallest and in *para* position to the largest values of ^1J(C,F) independent of the total number and the positions of the remaining fluorine atoms. The ^{13}C NMR spectra of tris(polyfluorophenyl)boroxins were not recorded because of the very low solubility of these compounds.

Experimental

The NMR spectra were recorded on the BRUKER spectrometers WP 80 SY (at 32 °C, ^{1}H at 80.13 MHz and ^{19}F at 75.39 MHz), AVANCE 300 (at 23 °C, ^{1}H at 300.13 MHz, ^{19}F at 282.40 MHz, ^{11}B at 96.29 MHz) and Avance DRX 500 (at 23 °C, ^{1}H at 500.13 MHz, ^{19}F at 470.59 MHz, ^{11}B at 160.46 MHz, and ^{13}C at 125.76 MHz). The chemical shifts are referenced to TMS (^{1}H, ^{13}C), $BF_3 \cdot OEt_2/CDCl_3$ 15 % v/v (^{11}B) and CCl_3F [^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)], respectively. The IR spectra were recorded on BRUKER IFS 66 and Vector 22 FT-spectrometers on KBr pellets (the data for the acids are reported with-

Table 4 $^{13}C\{^1H\}$ NMR spectra of fluorinated phenyl(dihydroxy)boranes $ArB(OH)_2$ in acetone-d_6

Aryl group		Chemical shifts, ppm						Coupling constants (C,F) [a], Hz
		C_1	C_2	C_3	C_4	C_5	C_6	
C_6F_5	**1**	110.54	148.45	138.08	142.50	138.08	148.45	(C^2,F^2) 243.0, (C^2,F^3) 15.7, (C^2,F^4) 3.7, (C^2,F^6) 9.6, (C^3,F^3) 248.0, (C^3,F^2) 19.2, (C^3,F^4) 12.6, (C^3,F^5) 5.1, (C^4,F^4) 251.6, (C^4,F^3) 13.7, (C^4,F^2) 6.1
2,3,4,5-C_6HF_4 [b]	**2**	118.76	151.37	140.82	141.96	147.44	116.66	(C^2,F^2) 246.1, (C^3,F^3) 250.8, (C^4,F^4) 252.8, (C^5,F^5) 246.0
2,3,4,6-C_6HF_4 [b]	**3**	110.20	153.64	137.64	152.90	101.97	159.93	(C^2,F^2) 245.2, (C^3,F^3) 245.8, (C^4,F^4) 249.0, (C^6,F^6) 242.8
2,3,5,6-C_6HF_4	**4**	116.47	147.92	146.56	107.96	146.56	147.92	(C^2,F^2) 242.0, (C^3,F^3) 246.7
2,4,6-$C_6H_2F_3$	**5**	108.80	166.48	100.54	164.85	100.54	166.48	(C^2,F^2) 245.3, (C^4,F^4) 247.8
3,4,5-$C_6H_2F_3$ [b]	**6**	131.98	118.62	151.64	141.77	151.64	118.62	(C^3,F^3) 248.6, (C^4,F^4) 251.3, (C^2,F^3) 14.4, (C^3,F^4) 9.5, (C^4,F^3) 15.5, (C^2,F^4) 4, (C^3,F^5) 2.4
2,6-$C_6H_2F_3$	**7**	112.67	166.00	111.64	132.61	111.64	166.00	(C^2,F^2) 243.2, (C^3,F^2) 22.1, (C^2,F^6) 14.6, (C^4,F^2) 10.1, (C^3,F^6) 6.1
2,4-$C_6H_2F_3$ [b]	**8**	117.75	168.33	103.93	165.64	111.90	138.68	(C^2,F^2) 248.5, (C^4,F^4) 250.1, (C^5,F^4) 20.1, (C^4,F^2) 12.8, (C^6,F^2) 10.4, (C^6,F^4) 10.4, (C^5,F^2) 3.6, (C^2,F^3) 29.3, (C^2,F^4) 24.3
4-C_6H_4F [b]	**9**	130.72	137.40	115.08	165.31	115.08	137.40	(C^4,F^4) 246.1, (C^3,F^4) 19.9, (C^2,F^4) 8

[a] Tentative assignment.

[b] Recorded in the presence of D_2O (3 equivalents).

out the ν(OH) range) or films on a 1 mm Si window. The samples of anhydrides were handled in a Braun glovebox MB-100G in an atmosphere of dry Argon. High resolution mass spectra were recorded on a Finnigan MAT 8200 spectrometer. Differential scanning calorimetry measurements were made with a Netzsch DSC 204 instrument. The samples were placed in aluminium pans with a pierced lid and measured in a temperature range of 20 − 330 °C. The elemental analyses were performed in the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry (Novosibirsk).

1,2,3,4-Tetrafluorobenzene (ABCR), 1-bromo-2,4,6-trifluorobenzene (ABCR), 1-bromo-2,6-difluorobenzene (ABCR), 1-bromo-4-fluorobenzene (Riedel-de Haen), 1,2,4,5-tetrafluorobenzene (Fluorochem), 1,2,3,5-tetrafluorobenzene (Fluorochem), 2.5 M *n*-BuLi in hexane (Aldrich) were used as supplied. Bromopentafluorobenzene was produced in the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry. 1-Bromo-2,4-difluorobenzene was produced from 2,4-difluoroaniline (Aldrich). $B(OCH_3)_3$ (Merck) was distilled over Na before use.

Pentafluorophenyl(dihydroxy)borane $C_6F_5B(OH)_2$ (**1**)

Pentafluorophenylmagnesium bromide [from bromopentafluorobenzene (9.88 g, 40 mmol) and magnesium (1 g, 41.2 mmol) in ether (80 ml)] was cooled with an ice-water bath and added in portions to the pre-cooled (ice-water) solution of $B(OMe)_3$ (6.07 g, 60 mmol) in ether (30 ml). The suspension was stirred at 0 − 4 °C for 1 h and then poured into 5 % HCl (100 ml). The organic layer was separated, the aqueous layer was extracted with ether (20 ml) and the combined extracts were dried over $MgSO_4$. After evaporation under reduced pressure pentafluorophenyl(dihydroxy)borane **1** (7.64 g, 90 %) was obtained as a light brownish solid. Recrystallization of **1** from hot toluene gave 4.29 g (51 %) of white needles.
$C_6H_2BF_5O_2$ (211.88): calculated C 34.01, H 0.95, F 44.83; found C 34.1, H 0.88, F 44.0 %.

IR $\tilde{\nu}$ (cm^{-1}): (film on Si) 3367 s, b (O-H), (KBr) 1651 m, 1527 s, 1488 vs, 1399 s, 1351 s, 1334 s, 1272 s, 1234 m, 1107 m, 1029 m, 978 s, 861 m, 799 m, 743 w, 673 w, 625 w, 606 m, 572 w.

2,3,4,5-Tetrafluorophenyl(dihydroxy)borane 2,3,4,5-$C_6HF_4B(OH)_2$ (**2**)

n-BuLi (2.5 M in hexane; 8.8 ml, 22 mmol) was added to a solution of 1,2,3,4-tetrafluorobenzene (3 g, 20 mmol) in ether (40 ml) at −70 to −75 °C. The solution was stirred for 1 h at −70 to −60 °C and then added to the cold (−70 °C) solution of trimethoxyborane (3.11 g, 30 mmol) in ether (40 ml). The mixture was kept for 1 h at < −60 °C and warmed to 15 − 18 °C within 1 h. After hydrolysis with 10 % HCl (50 ml) the organic layer was separated and the aqueous layer extracted with ether (2 x 10 ml). The combined extracts were dried over $MgSO_4$. The acid **2** (2.67 g, 68 %) was obtained after evaporation of the solvent under reduced pressure. Recrystallization of the crude product from toluene yielded white needles of **2**, 0.86 g (22 %).

MS (70 eV): calc. for $C_6H_3BF_4O_2$: 194.01623 (M^+); found M^+ 194.00744 m/z.
IR $\tilde{\nu}$ (cm^{-1}): (film on Si) 3197 s, b (O-H), 3071 w, 1641 m, 1626 w, 1526 m, 1473 s, 1428 sh, 1367 vs, 1351 s, 1229 m, 1199 w, 1095 m, 1016 m, 993 w, 884 m, 759 m, 753 m, 716 w, 631 m, 616 m, 551 w.

2,3,4,6-Tetrafluorophenyl(dihydroxy)borane 2,3,4,6-$C_6HF_4B(OH)_2$ (**3**)

n-BuLi (2.5 M in hexane; 12.8 ml, 32 mmol) was added dropwise to the solution of 1,2,3,5-tetrafluorobenzene (4.5 g, 30 mmol) in ether (60 ml) at −70 °C and was stirred for 1 h at this temperature before it was slowly transferred to the pre-cooled and stirred solution (−60 °C) of trimethoxyborane (4.67 g, 75 mmol) in ether (20 ml). After 1 h at −60 °C the reaction mixture was warmed to 20 °C within 1 h and hydrolyzed with 10 % HCl (20 ml). The organic phase was separated, the aqueous phase was extracted with ether (2 x 20 ml) and the combined extracts were dried over $MgSO_4$. After evaporation of the solvent 2,3,4,6-tetrafluorophenyl-(dihydroxy)borane (5 g, 85 %) was received. Recrystallization of **3** from hot toluene gave 4.23 g (73 %) of white needles.
$C_6H_3BF_4O_2$ (193.89): calculated C 37.17, H 1.56, F 39.19; found C 37.7, H 1.52, F 39.2 %.

IR $\tilde{\nu}$ (cm^{-1}): (KBr pellet) 3093 w (C-H), 1638 m, 1617 w, 1592 w, 1513 s, 1454 s, 1427 m, 1400 m, 1359 m, 1338 m, 1242 w, 1134 m, 1105 m, 1046 m, 1018 m, 874 m, 860 m, 799 m, 745 m, 693 w, 689 w, 619 w, 587 m, 576 w, 547 m.

2,3,5,6-Tetrafluorophenyl(dihydroxy)borane 2,3,5,6-$C_6HF_4B(OH)_2$ (**4**)

2,3,5,6-Tetrafluorophenyllithium was prepared from 1,2,4,5-tetrafluorobenzene (4.5 g, 30 mmol) and *n*-BuLi (2.5 M in hexane; 12.8 ml, 32 mmol) in ether (60 ml) at −70 to −60 °C and was slowly added to the cold (−70 °C) solution of trimethoxyborane (4.67 g, 45 mmol) in ether (30 ml). The mixture was stirred at −60 °C for 1 h, warmed to 15 °C within 1 h and poured into 5 % HCl (100 ml). The organic layer was separated, the aqueous layer was extracted with ether (2 x 10 ml) and the combined extracts were dried over $MgSO_4$. The solvent was distilled off to give 2,3,5,6-tetrafluorophenyl(dihydroxy)borane (4.67 g, 80 %). After recrystallization from hot toluene the acid **4** (2,77 g, 48 %) was obtained as white needles.
$C_6H_3BF_4O_2$ (193.89): calculated C 37.17, H 1.56, F 39.19; found C 36.8; H 1.60; F 39.2 %.

IR $\tilde{\nu}$ (cm^{-1}): (KBr pellet) 3100 w (C-H), 1829 w, 1715 w, 1650 w, 1616 w, 1484 vs, 1448 m, 1378 s, 1341 s, 1271 w, 1249 m, 1231 m, 1174 m, 1137 m, 1118 w, 1097 w, 1022 w, 927 s, 889 w, 858 m, 805 m, 738 m, 710 m, 692 m, 626 w, 502 w.

2,4,6-Trifluorophenyl(dihydroxy)borane 2,4,6-$C_6H_2F_3B(OH)_2$ (**5**)

n-BuLi in hexane (2.5 M; 9 ml, 22.5 mmol) was slowly added to the solution of 1-bromo-2,4,6-trifluorobenzene (4.5 g, 21.3 mmol) in ether (60 ml) at −60 °C and kept for 1 h at this temperature. The cold (−70 °C) solution of trimethoxyborane (3.34 g, 32 mmol) in ether (30 ml) was added and the reaction mixture was stirred for an additional 1 h at −60 °C followed by warming up to 20 °C within 1 h. After workup, as described before, 3.19 g (85 %) of **5** were obtained as a white solid. Recrystallization from hot toluene gave 2.35 g (63 %) of 2,4,6-trifluorophenyl(dihydroxy)borane.
$C_6H_4BF_3O_2$ (175.90): calculated C 40.97, H 2.29, F 32.40; found C 41.4, H 2.37, F 32.3 %.

IR $\tilde{\nu}$ (cm^{-1}): (KBr pellet) 3107 w (C-H), 2446 w, 2142 w, 1635 s, 1614 m, 1595 s, 1517 w, 1441 s, 1406 w, 1386 m, 1350 s, 1326 s, 1153 m, 1122 s, 1019 s, 998 m, 864 m, 854 m, 842 w, 799 m, 744 w, 696 w, 646 w, 612 w, 584 w, 537 m, 516 m.

3,4,5-Trifluorophenyl(dihydroxy)borane 3,4,5-$C_6H_2F_3B(OH)_2$ (**6**)

The Grignard reagent 3,4,5-$C_6H_2F_3MgBr$ was prepared from 4.22 g (20 mmol) of 1-bromo-3,4,5-trifluorobenzene and Mg (0.51 g, 21 mmol) in ether (35 ml). After cooling to 0 °C the reagent was added to the cold (0 °C) solution of $B(OMe)_3$ (3.11 g, 30 mmol) in ether (30 ml). The reaction mixture was maintained at 0 to 10 °C for 1 h, was allowed to warm up to 20 °C and poured into 10 % HCl (50 ml). The organic phase was separated, the aqueous phase was extracted with two portions of ether (2 x 10 ml) and the combined extracts were dried over $MgSO_4$. After evaporation under reduced pressure 3,4,5-trifluorophenyl(dihydroxy)borane (2.67 g), slightly contaminated by the corresponding anhydride, was obtained.

2,6-Difluorophenyl(dihydroxy)borane 2,6-$C_6H_3F_2B(OH)_2$ (7)

n-BuLi (2.5 M in hexane; 8 ml, 20 mmol) was slowly added to a solution of 2,6-difluorobromobenzene (3.86 g, 20 mmol) in ether (30 ml) at −60 °C. After stirring for 1 h at −60 to −70 °C the solution was added to the pre-cooled (−70 °C) and stirred solution of trimethoxyborane (3.11 g, 30 mmol) in ether (20 ml) within 30 minutes. The reaction mixture was stirred for 1 h at −70 to −60 °C, warmed up to 20 °C within 30 − 40 min. and finally hydrolyzed with 5 % HCl (20 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were dried over $MgSO_4$ and the solvent was distilled off under reduced pressure to yield 2.46 g (77 %) of acid **7**. Recrystallization from hot toluene gave 2,6-difluorophenyl(dihydroxy)borane (white shining plates, 0.83 g, 26 %).
$C_6H_5BF_2O_2$ (157.91): calculated C 45.64, H 3.19, F 24.06; found C 45.0, H 3.32, F 23.4 %.

IR $\tilde{\nu}$ (cm^{-1}): (KBr pellet) 3115 w, 3073 w (C-H), 2238 w, 1943 w, 1859 w, 1770 w, 1626 s, 1588 w, 1567 m, 1463 vs, 1418 m, 1397 s, 1372 w, 1346 s, 1256 m, 1218 m, 1152 m, 1121 m, 1065 m, 1026 m, 986 s, 881 w, 793 s, 737 w, 657 w, 628 m, 565 w, 540 m, 515 w.

*2,4-Difluorophenyl(dihydroxy)borane 2,4-$C_6H_3F_2B(OH)_2$ (**8**)*

2,4-Difluorophenyllithium was prepared from 1-bromo-2,4-difluorobenzene (3.86 g, 20 mmol) and *n*-BuLi (2.5 M in hexane; 8.8 ml, 22 mmol) in ether (40 ml) at −70 °C. The cold reagent was gradually added to the cold solution of trimethoxyborane (3.11 g, 30 mmol) in ether (40 ml). The reaction mixture was stirred at −60 °C for 1 h, allowed to warm to 15 °C within 1 h and hydrolysed with 5 % HCl (100 ml). The organic layer was separated, the aqueous layer was extracted with ether (2 x 10 ml) and the combined extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure and the solid residue was stored over water at 15 °C for 1 month to give acid **8** (2.69 g, 77 %).

IR $\tilde{\nu}$ (cm^{-1}): (film on Si) 3631 m, 3224 vs, b (O-H), 1614 m, 1589 w, 1473 s, 1443 s, 1409 s, 1369 s, 1339 s, 1295 w, 1264 m, 1231 w, 1196 s, 1150 vw, 1131 w, 1100 vw, 1045 m, 1005 m, 995 m, 883 vw, 858 m, 814 m, 742 m, 725 m, 686 vw, 677 vw, 645 vw, 629 m, 595 w, 568 w, 546 s, 512 w, sh, 453 w.

*Tris(pentafluorophenyl)boroxin ($C_6F_5BO)_3$ (**1a**)*

(Method A) A trap with pentafluorophenyl(dihydroxy)borane (63 mg, 0.30 mmol) was connected to a drying tube filled with Sicapent (P_4O_{10}/SiO_2). The borane was kept at 100 °C until a constant weight was achieved (2 − 2.5 h). The loss of mass was 5.4 mg (0.30 mmol of H_2O). The arylboroxin **1a** was obtained quantitatively.
(Method B) Thionyl chloride (100 mg, 0.84 mmol) was added to the solution of acid **1** (20 mg, 0.09 mmol) in ether (0.3 ml). Within a few minutes compound **1a** was precipitated. After removing the volatile products under reduced pressure **1a** was isolated in quantitative yield.

MS (70 eV): calc. for $C_{18}B_3F_{15}O_3$: 581.98874 (M$^+$); found M$^+$ 581.98869 m/z.
IR $\tilde{\nu}$ (cm^{-1}): (film on Si) 1675 vw, 1649 m, 1525 m, 1487 s, 1441 w, 1349 s, 1281 w, 1263 w, 1228 m, 1093 w, 984 s, 887 w, 860 vw, 768 w, 759 w, 709 w, 627 m, 577 w, 482 w.

*Tris(2,3,5,6-tetrafluorophenyl)boroxin (2,3,5,6-$C_6HF_4BO)_3$ (**4a**)*

(Method A) Compound **4a** (98 % yield) was prepared by the thermal dehydration of acid **4** (98 mg, 0.51 mmol).

(Method B) Compound **4a** was prepared from acid **4** (20 mg, 0.10 mmol) and $SOCl_2$ (100 mg. 0.84 mmol) in ether in quantitative yield.

MS (70 eV): calc. for $C_{18}H_3B_3F_{12}O_3$: 528.01699 (M$^+$); found M$^+$ 528.01641 m/z.
IR $\tilde{\nu}$ (cm^{-1}): (film on Si) 1643 w, 1614 vw, 1482 vs, 1377 m, 1342 s, 1302 w, 1269 w, 1244 w, 1231 w, 1172 m, 1138 w, 1119 w, 1097 w, 1019 w, b, 926 m, 890 w, 867 w, 857 m, 792 w, b, 757 w, 737 w, 710 w, 690 w, 677 w, 619 w, 506 vw, 489 vw.

*Tris(3,4,5-trifluorophenyl)boroxin (3,4,5-$C_6H_2F_3BO)_3$ (**6a**)*

(Method C) Compound **6a** was obtained by azeotropic treatment of acid **6** in toluene followed by crystallisation from boiling toluene in 56 % yield. Solid **6a** was stored over P_4O_{10}.
$C_{18}H_6B_3F_9O_3$ (473.67): calculated C 45.64, H 1.28, F 36.10; found C 46.2, H 1.29, F 36.6 %.

MS (70 eV): calc. for $C_{18}H_6B_3F_9O_3$: 474.04525 (M$^+$); found M$^+$ 474.04487 m/z.
IR $\tilde{\nu}$ (cm^{-1}): (KBr pellet) 3076 w (C-H), 1769 w, 1616 m, 1589 m, 1529 m, 1424 vs, 1360 vs, 1338 vs, 1293 m, 1217 s, 1038 s, 926 w, 879 m, 772 m, 747 m, 737 m, 713 w, 686 m, 622 m, 517 w. (film on Si) 3075 vw (C-H), 1767 vw, 1614 m, 1587 w, 1528 m, 1423 s, 1359 s, 1337 s, 1294 m, 1217 m, 1038 s, 926 w, 879 w, 771 m, 747 w, 737 w, 713 vw, 686 vw, 622 s, 516 w, 490 w.

*Tris(2,4-difluorophenyl)boroxin ($C_6H_3F_2BO)_3$ (**8a**)*

(Method C) Compound **8a** was obtained by azeotropic treatment of acid **8** in toluene followed by crystallisation from boiling toluene in 60 % yield. Solid **8a** was stored over P_4O_{10}.
$C_{18}H_9B_3F_6O_3$ (419.70): calculated C 51.51, H 2.16, F 27.16; found C 50.6, H 2.33, F 26.8 %.

IR $\tilde{\nu}$ (cm^{-1}): (film on Si) 1610 m, 1588 s, 1499 w, 1432 s, 1368 s, 1352 sh, 1308 m, 1259 s, 1226 m, 1137 m, 1109 m, 1071 w, sh, 964 m, 852 m, 817 w, 740 m, 675 m, 554 w, 523 m, 462 w.

*Tris(4-fluorophenyl)boroxin ($C_6H_4FBO)_3$ (**9a**)*

(Method C) Compound **9a** (1.96 g, 40 %) was obtained by azeotropic treatment of acid **9** in toluene followed by crystallisation from boiling toluene. Solid **9a** was stored over P_4O_{10}. **9** in a mixture with **9a** was prepared by the reaction of 4-fluorophenylmagnesium bromide [from 1-bromo-4-fluorobenzene (7 g, 41 mmol) and magnesium (1 g, 41.1 mmol)] with $B(OMe)_3$ (6.7 g, 64.5 mmol).
$C_{18}H_{12}B_3F_3O_3$ (365.73): calculated C 59.12, H 3.31, F 15.58; found C 58.8, H 3.24, F 15.7 %.

MS (70 eV): calc. for $C_{18}H_{12}B_3F_3O_3$: 366.10177 (M$^+$); found M$^+$ 366.10252 m/z.
IR $\tilde{\nu}$ (cm^{-1}): (KBr pellet) 3050 w (C-H), 2429 w, 2235 w, 2150 w, 2031 w, 1913 w, 1783 w, 1599 s, 1511 w, 1405 s, 1368 s, 1350 s, 1306 m, 1219 m, 1155 m, 1094 m, 1016 w, 945 w, 835 m, 814 w, 742 m, 683 w, 627 w, 527 m, 504 w.

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft, the Russian Foundation for Basic Research, and the Fonds der Chemischen Industrie.

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