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Syntheses of lipophilic tetraarylborate ions substituted with many perfluoroalkyl groups and their stability under acid conditions

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This paper is dedicated to Professor Paul Tarrant on the occasion of his 85th birthday

Abstract

Syntheses are investigated on several new kinds of perfluoroalkyl-substituted tetraarylborate ions such as tetrakis(3,5-bis(nonafluorobutyl)phenyl)borate, tetrakis(3,5-bis(heptafluoro-2-propyl)phenyl)borate (**PFPB**), tetrakis(3-(heptafluoro-2-propyl)-1-(trifluoromethyl)phenyl)borate, and tetrakis(3-(heptafluoro-2-propyl)phenyl)borate. Solubilities of tetramethylammonium tetraarylborates in some hydrophobic halocarbon solvents and rate constants of acid-catalyzed decomposition of the tetraarylborate ions in methanolic sulfuric acid solutions and in dichloromethane/aqueous sulfuric acid two-phase system are determined. Trifluoromethyl- and perfluoroalkyl-substituent effects on the lipophilicity and chemical stability of the tetraarylborate ions are discussed in comparisons with a range of those described previously.

Keywords: Weakly coordinating anions; Perfluoroalkyl-substituted tetraarylborate ions; Syntheses; Lipophilicity; Stability

1. Introduction

With the purpose of obtaining lipophilic and bulky but still stable anions, we have first synthesized tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**TFPB**) (**1**) [1] and several tetraphenylborate derivatives substituted with many trifluoromethyl groups, which efficiently incorporate various cations into hydrophobic solution phases as ion pairs and are successfully applied as ion-pair extracting agents [2,3]. **TFPB** is a characteristic stable anion, whose anionic center is tetrahedrally covered by four bulky aryl groups with many trifluoromethyl groups and able to enforce hydrophilic cations to be incorporated into a less polar organic solution phase in the form of stable ion pairs. By taking advantage of such merits of the lipophilic and stable borate anions, the primarily extracted cationic species can be converted to various higher-order electrophilic reagents, with which novel reaction processes have been developed [4,5]. **TFPB** is now widely recognized as an excellent example of a weakly coordinating anion [6,7] or superweak anions [8] especially as a useful counter anion of electrophilic cationic transition metal complexes.

In continuation of our previous work [9], this paper deals with the syntheses and chemical properties of tetraphenylborates substituted with one or two perfluoroalkyl groups on each phenyl group: Tetrakis(3,5-bis(nonafluorobutyl)phenyl)borate (**2**), tetrakis(3,5-bis(heptafluoro-2-propyl)phenyl)borate (**PFPB**) (**3**), tetrakis(3-(heptafluoro-2-propyl)-1-(trifluoromethyl)phenyl)borate (**4**), and tetrakis(3-(heptafluoro-2-propyl)phenyl)borate (**5**) (Fig. 1).

2. Results and discussion

2.1. Preparation of intermediates for the borate syntheses

Perfluoroalkyl groups such as heptafluoro-2-propyl and nonafluorobutyl substituents could be introduced to a benzene ring by coupling reactions of the corresponding

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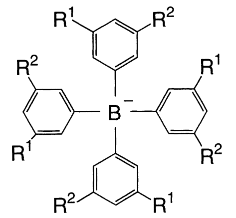


TFPB (1)	$R^1 = CF_3$, $R^2 = CF_3$
2	$R^1 = R^2 = (CF_2)_3CF_3$
PFPB (3)	$R^1 = R^2 = CF(CF_3)_2$
4	$R^1 = CF_3$, $R^2 = CF(CF_3)_2$
5	$R^1 = H$, $R^2 = CF(CF_3)_2$

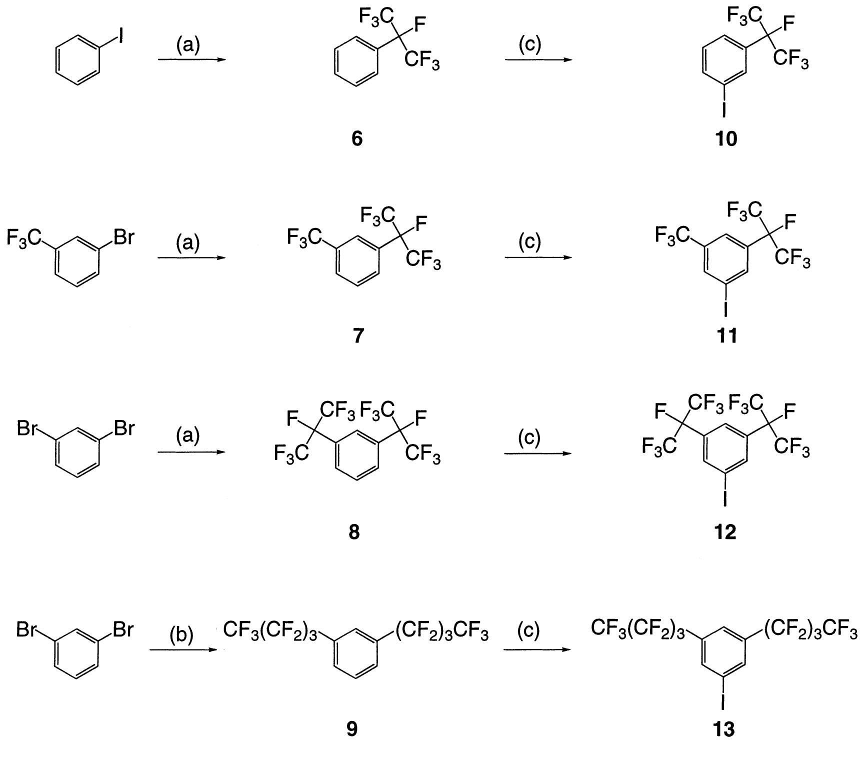
Fig. 1. Perfluoroalkyl-substituted tetraarylborates.

aryl iodides or bromides with the desired perfluoroalkyl iodides in the presence of an excess amount of activated copper [10,11] to afford perfluoroalkyl-substituted benzene derivatives such as (heptafluoro-2-propyl)benzene (**6**), 3-(heptafluoro-2-propyl)-1-(trifluoromethyl)benzene (**7**), 1,3-bis(heptafluoro-2-propyl)benzene (**8**), and 1,3-bis(nonafluorobutyl)benzene (**9**) in satisfactory yields. Dimethylformamide (DMF) was most favorable as solvent for higher yields of products compared to dimethylsulfoxide (DMSO).

Perfluoroalkyl-substituted iodobenzene derivatives (Scheme 1) were synthesized as precursors for Grignard reagents by direct iodination of the perfluoroalkyl-substituted benzene derivatives with iodine in 20% fuming sulfuric acid [12] to give 3-(heptafluoro-2-propyl)iodobenzene (**10**), 3-(heptafluoro-2-propyl)-5-(trifluoromethyl)iodobenzene (**11**), 3,5-bis(heptafluoro-2-propyl)iodobenzene (**12**), and 3,5-bis(nonafluorobutyl)iodobenzene (**13**), respectively, in fair yields.

2.2. Syntheses of perfluoroalkyl-substituted tetraarylborates

The method and reaction conditions for the syntheses of perfluoroalkyl-substituted tetraarylborates (Scheme 2) are basically the same as previously described [9]. Grignard reagents were prepared in ether from the perfluoroalkyl-substituted iodo- or bromo-benzenes in the presence of 10% molar amount of butylmagnesium bromide as initiating catalyst, which was necessary for the preparation of the perfluoroalkyl-substituted phenyl Grignard reagents. A 25% excess amount of the Grignard reagent was added into ether solution of boron trifluoride etherate and the mixture was refluxed for sufficient time to complete the reaction. The resulting tetraarylborate derivatives, **2**–**5**, were easily isolated as corresponding tetramethylammonium salts. Tetrakis(3-(trifluoromethyl)phenyl)borate salt (**14**) was also prepared as one of the reference compounds according to the literature [13] (Table 1).



(a) $ICF(CF_3)_2 + Cu$ / DMF , 90˚C
(b) $I(CF_2)_3CF_3 + Cu$ / DMF , 100˚C
(c) I_2 / 20% fum.H_2SO_4

Scheme 1. Syntheses of perfluoroalkyl-substituted iodobenzenes.

$$\mathrm{ArX} \xrightarrow{\mathrm{Mg,\ RMgX'\ (cat.)\ /\ Et_2O}} [\mathrm{ArMgX}]$$

$$\xrightarrow[\mathrm{(2)\ Na_2CO_3\ aq}]{\mathrm{(1)\ BF_3\ OEt_2\ /\ Et_2O}} \mathrm{NaBAr_4} \xrightarrow{\mathrm{Me_4NCl\ /\ MeOH}} \mathrm{Me_4NBAr_4}$$

Scheme 2. Syntheses of tetraarylborates.

Table 1
Preparation of tetramethylammonium perfluoroalkyl-substituted tetraarylborates

Borate	Substituent[a]		Yield (%)	m.p. (°C)
	R^1	R^2		
2	$(CF_2)_3CF_3$	$(CF_2)_3CF_3$	62	151–152 (decomp.)
PFPB (**3**)	$CF(CF_3)_2$	$CF(CF_3)_2$	50	260–263 (decomp.)
4	CF_3	$CF(CF_3)_2$	64	146–147
5	H	$CF(CF_3)_2$	62	158–160
14	H	CF_3	24	167–168 [13]

[a] For R^1 and R^2, see Fig. 1.

2.3. Properties of tetraarylborate derivatives

2.3.1. Solubility

Lipophilicity is one of the most important properties of an ion-pair extracting agent. As a parameter of this property, the solubilities of tetraarylborates were measured in a range of hydrophobic organic solvents.

TFPB (**1**) salt is much more soluble in organic solvents than its unsubstituted tetraphenylborate (**TPB**) (**15**) counterpart, which is due to the substitution by lipophilic trifluoromethyl groups on each phenyl ring. Table 2 shows the solubilities of some borates including those previously described [9] in polychloromethane and polyfluorocarbon solvents. One can readily notice that a branched side chain causes increasing solubility, while a straight one depresses solubility in spite of the increasing number of lipophilic difluoromethylene units, which seems indicative that the solubility of tetraarylborate in a hydrophobic solvent is closely correlated with the number of trifluoromethyl groups and at the same time with the bulkiness of the substitutent as a whole.

An interesting feature is that in a polyfluorinated solvent, $(CBrF_2)_2$, **PFPB** (**3**) is approximately 100-times more soluble than **TFPB** (**1**). An increasing number of trifluoromethyl substituents enhances solubility in the polyfluorinated solvent, but not always so in chloromethane solvents.

A similar correlation can be observed when the solubility of **TFPB** (**1**) is compared with those of the reference borates, **4**, **14**, **17**, and **18**, of which each phenyl group is unsymmetrically substituted with the combination of trifluoromethyl and various trifluoromethylated groups. Increase in the solubility of borate **5** containing a perfluoroisopropyl group in the polyfluorinated solvent is also remarkable when compared with that of borate **14** containing a trifluoromethyl group.

The observed correlation seems of interest in connection with the interaction among the fluorine substituents on the solute and solvent molecules, which might be useful for designing molecules soluble in less polar polyfluorinated solvents.

2.3.2. Chemical stability against acid

Another effect of trifluoromethyl substituent was shown in the increased chemical stability of **TFPB** (**1**), especially against acid. **TPB** (**15**) is known to decompose easily under acid conditions by rate-determining electrophilic attack of proton to the phenyl ring at the ipso carbon to give benzene via a Wheland-type intermediate [14,15]. Beside the poor lipophilicity of **TPB** (**15**), this is another defect with respect to less versatile applications such as to an ion-pair extractant under acid conditions and an electrophilic metal ion catalyst. Especially, the lability under acid conditions is a fatal one as an anionic PTC catalyst; i.e., in the anionic PTC process to promote the electrophilic reactions of cationic reagents in an organic phase, oxonium ion or protonated species is a primary by-product which ion-pairs with the anionic catalyst in the same phase. **TPB** (**15**) ion, when used as the catalyst, is decomposed autocatalytically [16,17]. Similarly, **TPB** is not an effective counter anion for a highly electrophilic metal ion catalyst which autocatalytically

Table 2
Solubility of polyfluoroalkyl-substituted tetraarylborates[a]

Borate	Substituent		Solubility in solvent (mol dm^{-3})		
	R^1	R^2	CH_2Cl_2	$CHCl_3$	$(CBrF_2)_2$
TFPB (1)	CF_3	CF_3	2.0×10^{-2}	1.4×10^{-4}	$<1.4 \times 10^{-5}$
HFPB (16)	$C(CF_3)_2OCH_3$	$C(CF_3)_2OCH_3$	2.2×10^{-1}	3.6×10^{-3}	4.5×10^{-4}
PFPB (3)	$CF(CF_3)_2$	$CF(CF_3)_2$	1.2×10^{-1}	5.0×10^{-4}	1.8×10^{-3}
2	$(CF_2)_3CF_3$	$(CF_2)_3CF_3$	6.2×10^{-4}	1.3×10^{-5}	5.8×10^{-5}
14	H	CF_3	1.4×10^{-1}	7.5×10^{-4}	$<2.2 \times 10^{-7}$
4	$CF(CF_3)_2$	CF_3	1.4×10^{-1}	6.6×10^{-4}	2.0×10^{-4}
17	$C(CF_3)_2OCH_3$	CF_3	7.7×10^{-2}	3.1×10^{-3}	2.2×10^{-4}
18	$C(CF_3)_2OCH_2CF_3$	CF_3	4.0×10^{-3}	1.8×10^{-5}	1.4×10^{-3}
5	H	$CF(CF_3)_2$	4.7×10^{-2}	7.6×10^{-4}	1.3×10^{-4}

[a] Dielectric constant at 25°C: CH_2Cl_2 (8.93), $CHCl_3$ (4.81), $(CBrF_2)_2$ (4.81).

Table 3
Stability of polyfluoroalkyl-substituted tetraarylborates under acid two-phase conditions

Borate	Substituent		Pseudo first-order rate const. $k'_1/\mathrm{s}^{-1} \times 10^4$ at 27°C			
	R^1	R^2	Acid concn./mol dm^{-3} H_2SO_4 aq			
			0.5	3.0	5.1	10.3
TFPB(1)	CF_3	CF_3	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]
HFPB(16)	$C(CF_3)_2OCH_3$	$C(CF_3)_2OCH_3$	1.45	5.23	87.1	d[b]
17	$C(CF_3)_2OCH_3$	CF_3	n.d.[a]	1.18	2.96	d[b]
18	$C(CF_3)_2OCH_2CF_3$	CF_3	n.d.[a]	n.d.[a]	0.32	2.08

[a] Not decomposed.
[b] Immediately decomposed.

decomposes **TPB** ion by metal-ion promoted protonation or oxidation. An efficient anionic PTC catalyst, therefore, requires its higher chemical stability under acid conditions in addition to its high lipophilicity.

The pseudo-first-order rate constants were obtained in the decomposition of tetraarylborates under dichloromethane/aqueous sulfuric acid two-phase conditions by monitoring the formation of arenes by gas-chromatography (Table 3). Under these two-phase conditions, when the concentration of aqueous sulfuric acid is increased, then the activity of oxonium ion incorporated by the borate ion as an ion pair into the organic phase is increased due to less hydration of oxonium ion, to promote the decomposition of the counter borate ion [4].

The results in Table 3 indicate that the durabilities of the borates under acid conditions decrease in the order of

TFPB(1) > **18** > **17** > **16**,

in accordance with the order of electron-withdrawing ability of the meta-substituents [18],

$$CF_3 > C(CF_3)_2OCH_2CF_3 > C(CF_3)_2OCH_3.$$

Obviously, the Wheland intermediate formed by rate-limiting protonation to the borate ion is destabilized by the electron-withdrawing meta-substituents to suppress the decomposition.

On the other hand, the pseudo-first-order rate constants of the acid-catalyzed decomposition of tetraarylborates were obtained also in homogeneous aqueous methanolic sulfuric solution by monitoring the decrease in ^{19}F-NMR signal intensities of the remained tetraarylborates (Table 4).

Even under more sever acid conditions, **TFPB** (**1**) remain completely intact, while **PFPB** (**3**) decomposes slowly under the same acid conditions; i.e. the stabilizing effect of trifluoromethyl group is much greater than that of perfluoroisopropyl group, when each phenyl group of the borates is symmetrically disubstituted at 3,5-positions.

In a series of singly substituted derivatives the trifluoromethyl-substituted borate **14** is only three times more stable in terms of decompostion-rate constant than the perfluoroisopropyl-substituted homologue **5** in parallel to their σ_m values: 0.43 and 0.37 for trifluoromethyl- and perfluoroisopropyl substituents, respectively. Thus, one would need to presume some additional effects to explain the extreme stability of **TFPB** (**1**), which are still under investigation.

Comparison of the rate constants of the decomposition of **PFPB** (**3**) and **HFPB** (**16**) indicates that the introduction of a methoxyl group onto the isopropyl chain in place of a tertiary fluorine atom is not favorable as far as the stability under acid conditions is concerned, which might be readily understood in terms of the inductive effects (σ_I values) of

Table 4
Stability of polyfluoroalkyl-substituted tetraarylborates under acid homogeneous solutions.

Borate	Substituent		Pseudo first-order rate const. (k'_1/min^{-1} at 25°C)	
	R^1	R^2	Acid conditions	
			[I][a]	[II][b]
TFPB(1)	CF_3	CF_3	n.d.[c]	n.d.[c]
PFPB(3)	$CF(CF_3)_2$	$CF(CF_3)_2$	n.d.[c]	8.2×10^{-5}
5	H	$CF(CF_3)_2$	3.7×10^{-3}	d[d]
14	H	CF_3	1.4×10^{-3}	d[d]
HFPB(16)	$C(CF_3)_2OCH_3$	$C(CF_3)_2OCH_3$	n.d.[c]	2.8×10^{-3}

[a] Acid conditions: [I]; 3.1 mol dm^{-3} H_2SO_4 in MeOH + 9% water.
[b] Acid conditions: [II]; 3.6 mol dm^{-3} H_2SO_4 in MeOH.
[c] Not decomposed.
[d] Immediately decomposed.

fluorine- and methoxyl substituents, whose σ_I values are 0.50 and 0.27, respectively.

3. Experimental

^{1}H-, ^{13}C-, and ^{19}F-NMR and mass spectra were obtained on the corresponding spectrometers in similar manners as described previously [9]. Iodobenzene, 1,3-dibromobenzene, 3-(trifluoromethyl)bromobenzene, heptafluoro-2-iodopropane, and nonafluoro-1-iodobutane are commercially available reagents. All the starting compounds were used after purification by appropriate methods.

3.1. Preparation of activated copper powder

Into an aqueous solution (350 ml) of cupric sulfate pentahydrate (100 g, 0.29 mol) was added portionwise zinc powder (35 g, 0.54 mol) with vigorous stirring until the aqueous layer discolored. Aqueous supernatant was discarded and residual zinc metal was removed by treating with 1 mol dm^{-3} hydrochloric acid. Precipitated copper powder was collected by decantation, washed with 1 mol dm^{-3} hydrochloric acid, deionized water, methanol, ethanol, acetone, and ether, successively, and dried under reduced pressure. The activated copper powder was stored under a nitrogen atmosphere [19].

3.2. Copper-catalyzed coupling of arylhalide with perfluoroalkyl iodide

3.2.1. Typical procedure 3-(Heptafluoro-2-propyl)-(trifluoromethyl)benzene (*7*)

Into a mixture of 3-(trifluoromethyl)bromobenzene (15.00 g, 66.7 mmol) and activated copper powder (13.88 g, 218 mmol) in DMF (80 ml) was added heptafluoro-2-iodopropane (27.00 g, 91.2 mmol) at room temperature with vigorous stirring. The resulting mixture was kept stirred for an additional 15 h at 90°C. The reaction mixture was diluted with water and filtered off. Combined ethereal extracts from the filtrate were washed with water, 2 mol dm^{-3} hydrochloric acid, and saturated aqueous sodium chloride, successively. After usual work-up, the crude product was fractionated by distillation, to afford a colorless oil **7** boiling at 56°C/30 torr. (13.18 g, 63% yield). ^{1}H-NMR: $\delta = 7.9$–7.4 ppm (br, arom., 4H). ^{19}F-NMR: $\delta = 98.86$ (s, CF_3, 3F), 86.26 (d, $J = 7.3$ Hz, $CF(CF_3)_2$, 6F), and -20.58 ppm (sep, $J = 7.3$ Hz, $CF(CF_3)_2$, 1F).

3.2.2. 1,3-Bis(heptafluoro-2-propyl)benzene (*8*)

The reaction of 1,3-dibromobenzene (10.17 g, 43.1 mmol) with heptafluoro-2-iodopropane (33.21 g, 112 mmol) in the presence of activated copper (17.62 g, 276 mmol) in DMF (80 ml) at 90°C for 44 hr afforded a colorless oil **8** (11.88 g, 67% yield) boiling at 56°C/20 torr (lit. [9], 72% yield, bp 146–148°C). ^{1}H-NMR: $\delta = 7.9$–7.4 ppm (br, arom., 4 H). ^{19}F-NMR: $\delta = 86.22$ (d, $J = 7.3$ Hz, $CF(CF_3)_2$, 6F) and -20.58 ppm (sep, $J = 7.3$ Hz, $CF(CF_3)_2$, 1F). MS: *m/z* (rel. intensity) = 414(M^+), 395, and 345. Obsd. accurate *m/z* = 414.0089. Calcd. for $C_{12}H_4F_{14} = 414.0089$.

3.2.3. 1,3-Bis(nonafluorobutyl)benzene (*9*)

The reaction of 1,3-dibromobenzene (9.75 g, 39.2 mmol) with heptafluoro-2-iodopropane (40.72 g, 118 mmol) in the presence of activated copper (17.40 g, 274 mmol) in DMF (60 ml) under an argon atmosphere at 100°C for 44 h afforded a colorless oil **9** (14.20 g, 70% yield) boiling at 70°C/4.5 torr. ^{1}H-NMR: $\delta = 7.9$–7.4 ppm (br, arom., 4H). ^{19}F-NMR: $\delta = 80.81$ (br-tr, CF_3, 6F), 50.52 (br-tr, CF_2-1, 4F), 39.16 (m, CF_2-2, 4F), and 36.32 ppm (br-tr, CF_2-3, 4F). MS: *m/z* (rel. intensity) = 514(M^+), 495, 346, and 345.

3.2.4. (Heptafluoro-2-propyl)benzene (*6*)

The reaction of iodobenzene (14.65 g, 71.8 mmol) with heptafluoro-2-iodopropane (27.62 g, 93.3 mmol) in the presence of activated copper (11.87 g, 186.8 mmol) in DMF (50 ml) yielded the corresponding colorless oil **6** (11.61 g, 66% yield) boiling at 125°C (lit. [11], 54% yield, bp 124–124.5°C). ^{1}H-NMR: $\delta = 7.7$–7.3 ppm (br, arom., 5H). ^{19}F-NMR: $\delta = 86.14$ (d, $J = 7.3$ Hz, $CF(CF_3)_2$, 6F) and -20.58 ppm (sep, $J = 7.3$ Hz, $CF(CF_3)_2$, 1F). MS: *m/z* (rel. intensity) = 246(M^+), 177, 127, 77($C_6H_5{}^+$). Obsd. accurate *m/z* = 246.0280. Calcd. for $C_9H_5F_7 = 246.0279$.

3.3. Direct iodination

3.3.1. Typical procedure 3,5-Bis(heptafluoro-2-propyl)iodobenzene (*12*)

Into a dark solution of iodine (1.04 g, 4.1 mmol) in 20% fuming sulfuric acid (15 ml) was added dropwise 3,5-bis(heptafluoro-2-propyl)benzene (**8**) (3.10 g, 7.5 mmol) over 2 h at room temperature with vigorous stirring. The resulting mixture was kept stirring for an additional 14 h at room temperature and subsequently for 10 h at 65°C until the starting substance disappeared in the gas-chromatographic monitoring, and then poured portionwise into crashed ice (100 g). Separated dark oil was extracted repeatedly with ether, and the combined extracts were washed with 10% aqueous sodium hydrogen sulfite, saturated aqueous sodium hydrogen carbonate, water, and saturated aqueous sodium chloride, successively. The ether solution was dried over sodium sulfate and evaporated to give oily residue, which was fractionated under reduced pressure, to afford a colorless oil **12** boiling at 56.0°C/2.0 torr (2.92 g, 72% yield). ^{1}H-NMR: $\delta = 8.2$–8.0 (br, arom., 2H) and 7.9–7.6 ppm (br, arom., 1H). ^{19}F-NMR: $\delta = 86.34$ (d, $J = 7.3$ Hz, $CF(CF_3)_2$, 12F) and -20.34 ppm (sept, $J = 7.3$ Hz, $CF(CF_3)_2$, 2F). MS: *m/z* (rel. intensity) = 540(M^+). Obsd. accurate *m/z* = 539.9057. Calcd. for $C_{12}H_3F_{14}I = 539.9057$.

*3.3.2. 3-(Heptafluoro-2-propyl)iodobenzene (**10**)*

By the iodination of the starting compound **6** (3.0 g, 12.2 mmol) with iodine (1.7 g, 6.7 mmol) in 20% fuming sulfuric acid (20 ml) was isolated the corresponding product **10** (1.76 g, 39% yield) as a colorless oil boiling at 66/8.0 torr. ^{1}H-NMR: $\delta = 8.2$–7.0 ppm (m, 4H, arom.). ^{19}F-NMR: $\delta = 86.22$ (d, $J = 7.3$ Hz, $CF(CF_3)_2$, 6F) and -20.65 ppm (sept, $J = 7.3$ Hz, $CF(CF_3)_2$, 1F). MS: *m/z* (rel. intensity) = 372(M^+), 303, 253. Obsd. accurate *m/z* = 371.9247. Calcd. for $C_9H_4F_7I = 371.9247$.

*3.3.3. 3-(Heptafluoro-2-propyl)-5-(trifluoromethyl)-iodobenzene (**11**)*

From the reaction of the starting compound 7 (3.35 g, 10.7 mmol) and iodine (1.62 g, 6.4 mmol) was isolated the corresponding iodide **11** (2.09 g, 45% yield) as a colorless oil boiling at 50°C/3.0 torr. ^{1}H-NMR: $\delta = 8.2$–8.0 (br, arom., 1H) and 7.9–7.6 ppm (br, arom., 2H). ^{19}F-NMR: $\delta = 98.66$ (s, CF_3, 3F), 86.34 (d, $J = 7$ Hz, $CF(CF_3)_2$, 6F), and -20.34 ppm (m, $J = 7$ Hz, $CF(CF_3)_2$, 1F). MS: *m/z* (rel. intensity) = 440(M^+), 371, 321. Obsd. accurate *m/z* = 439.9120. Calcd. for $C_{10}H_3F_{10}I = 439.9121$.

*3.3.4. 3,5-Bis(nonafluoro-1-butyl)iodobenzene (**13**)*

From the reaction of the starting compound **9** (14.13 g, 27.5 mmol) and iodine (4.98 g, 19.6 mmol) in 20% fuming sulfuric acid (46 ml) was isolated the corresponding iodide **13** (13.75 g, 78% yield) as a colorless oil boiling at 80°C/2.0 torr, which solidified to sublimable colorless crystals melting at 50–51°C. ^{1}H-NMR: $\delta = 8.2$–8.0 (br, arom., 2H) and 7.8–7.6 ppm (br, arom., 1H). ^{19}F-NMR: $\delta = 80.80$ (br-tr, CF_3, 6F), 50.43 (br-tr, CF_2-1, 4F), 39.41 (m, CF_2-2, 4F), and 36.29 ppm (br-tr, CF_2-3, 4F). MS: *m/z* (rel. intensity) = 540(M^+).

3.4. Syntheses of tetraarylborates

*3.4.1. Typical procedure Tetramethylammonium tetrakis(3,5-bis(heptafluoro-2-propyl)phenyl)borate (**PFPB**) (**3**)*

A mixture of magnesium and butylmagnesium bromide (initiating catalyst) which was prepared from butyl bromide (0.030 g, 0.22 mmol) and magnesium turnings (0.22 g, 9.05 mmol) in freshly distilled dry ether (1.5 ml) under an argon atmosphere, was diluted with an additional 1.5 ml of dry ether and cooled on an ice bath. Into the cold mixture was slowly added an ethereal solution (15 ml) of 3,5-bis(heptafluoro-2-propyl)iodobenzene (**12**) (4.80 g, 8.89 mmol). The reaction mixture was kept stirred for an additional 3 h to complete the reaction. The resulting Grignard reagent was chilled to −40°C, and boron trifluoride etherate (252 mg, 1.78 mmol) in dry ether (5 ml) was added dropwise so slowly that the temperature was kept not higher than −40°C. The reaction mixture was kept stirred without a cold bath, to be warmed by itself up to room temperature, then heated under reflux for an additional 36 h. The resulting mixture was quenched by the addition of saturated aqueous sodium hydrogen carbonate (20 ml). Precipitates were removed by filtration and washed with ether, and an aqueous filtrate was extracted with ether repeatedly. An ethereal filtrate, washings, and extracts were combined and worked up as usual. The brown crude product was fractionated on an activated alumina column by elution with dichloromethane and methanol, successively. The fraction eluted with methanol was sonicated after the addition of methanolic tetramethylammonium chloride, and then evaporated off. The solid residue was dispersed in water and the mixture was extracted with dichloromethane. The extract was evaporated off, and a residual solid was recrystallized from a dichloromethane-hexane mixture, to yield colorless crystals of tetramethylammonium tetrakis(3,5-bis(heptafluoro-2-propyl)phenyl)borate (**3**) (1.55 g, 50% yield) melting at 260–263°C. ^{1}H-NMR(CD_3CN): $\delta = 7.3$–7.6 (br-s, arom., 12H) and 2.14 ppm (s, $N(CH_3)_4$, 12H). ^{19}F-NMR(CD_3CN): $\delta = 87.43$ (d, $J = 6.3$ Hz, $CF(CF_3)_2$, 48F) and -18.86 ppm (sept, $J = 6.3$ Hz, $CF(CF_3)_2$, 8F). ^{13}C-NMR(CD_3CN): $\delta = 162.32$ (q, $J = 49.9$ Hz, arom. C-1), 135.32 (d, $J = 7.8$ Hz, arom. C-2,6), 126.49 (dsept, $J = 19.6$ and 2.9 Hz, arom. C-3,5), 121.53 (dq, $J = 27.4$ and 285.6 Hz, $CF(CF_3)_2$), 119.02 (d, $J = 13.7$ Hz, arom. C-4), 92.61 (dsept, $J = 201.5$ and 33.3 Hz, $CF(CF_3)_2$), and 56.25 ppm (t, $J_{N\text{–}C} = 3.9$ Hz, NCH_3).

*3.4.2. Tetramethylammonium tetrakis(3,5-bis(nonafluorobutyl)phenyl)borate (**2**)*

The Grignard reagent, which was prepared from 3,5-bis(nonafluorobutyl)iodobenzene (**13**) (13.75 g, 21.5 mmol) and magnesium (0.52 g, 21.4 mmol) in the presence of butylmagnesium bromide (0.66 mmol), was reacted in situ with boron trifluoride etherate (669 mg, 4.71 mmol). Work-up as usual yielded colorless crystals of tetramethylammonium tetrakis(3,5-bis(nonafluoro-1-butyl)phenyl)borate (**2**) (6.24 g, 62% yield) melting at 151–152°C (from ethyl acetate-hexane). ^{1}H-NMR(CD_3OD): $\delta = 7.7$–7.3 (br, arom., 12H) and 3.21 ppm (s, $N(CH_3)_4$, 12H). ^{19}F-NMR(CD_3OD): $\delta = 82.30$ (t-like m, $J = 9.8$ Hz, CF_3, 12F), 52.60 (t-like m, $J = 12.2$ Hz, CF_2-1, 8F), 40.37 (br-m, CF_2-2, 8F), and 38.18 ppm (t-like m, J = 12.2 Hz, CF_2-3, 8F).

*3.4.3. Tetramethylammonium tetrakis(3-(heptafluoro-2-propyl)-5-(trifluoromethyl)-phenyl)borate (**4**)*

The Grignard reagent, which was prepared from 3-(heptafluoro-2-propyl)-5-(trifluoromethyl)iodobenzene (**11**) (1.99 g, 4.5 mmol) and magnesium (0.13 g, 5.3 mmol) in the presence of butylmagnesium bromide (0.4 mmol), was reacted in situ with boron trifluoride etherate (137 mg, 1.0 mmol). Work-up as usual yielded colorless crystals of tetramethylammonium tetrakis(3-(heptafluoro-2-propyl)-5-(trifluoromethyl)phenyl)borate (**4**) (0.83 g, 64% yield) melting at 146–147°C (from dichloromethane-hexane). ^{1}H-NMR(CD_3OD): $\delta = 7.7$–7.4 (br, arom., 12H) and

3.20 ppm (s, $N(CH_3)_4$, 12H). ^{19}F-NMR(CD_3OD): $\delta = -18.78$ (sept, $J = 7$ Hz, $CF(CF_3)_2$, 4H), 87.75 (d, $J = 7$ Hz, $CF(CF_3)_2$, 24F) and 100.77 ppm (s, CF_3, 12F). ^{13}C-NMR(CD_3OD): $\delta = 162.87$ (q, $J = 49.9$ Hz, arom. C-1), 136.96 (s, arom. C-6), 134.75 (s, arom. C-2), 130.77 (q, $J = 32.3$ Hz, arom. C-5), 126.62 (d, $J = 19.6$ Hz, arom. C-3), 125.88 (q, $J = 271.9$ Hz, Ar-CF_3), 122.00 (dq, $J = 27.4$ and 284.6 Hz, $CF(CF_3)_2$), 118.86 (d, $J = 11.7$ Hz, arom. C-4), 93.04 (dsep, $J = 201.5$ and 32.3 Hz, $CF(CF_3)_2$), and 55.92 ppm (t, $J_{C–N}) = 3.9$ Hz, NCH_3).

*3.4.4. Tetramethylammonium tetrakis(3-(heptafluoro-2-propyl)phenyl)borate (**5**)*

The Grignard reagent, which was prepared from 3-heptafluoroisopropyliodobenzene (**10**) (4.07 g, 10.9 mmol) and magnesium (0.32 g, 13.1 mmol) in the presence of butylmagnesium bromide (1.1 mmol), was reacted in situ with boron trifluoride etherate (317 mg, 2.2 mmol). The reaction mixture was heated under reflux for 48 h, and then worked up as above to yield colorless crystals of tetramethylammonium tetrakis(3-(heptafluoro-2-propyl)phenyl)borate (**5**) (1.48 g, 62% yield) melting at 158–160°C (from dichloromethane-hexane). ^{1}H-NMR (CD_2Cl_2): $\delta = 7.6$–7.0 (br, arom., 16H) and 2.51 ppm (s, $N(CH_3)_4$, 12H). ^{19}F-NMR (CD_2Cl_2): $\delta = 86.57$ (d, $J = 7$ Hz, $CF(CF_3)_2$, 24F), and -19.83 ppm (sept, $J = 7$ Hz, $CF(CF_3)_2$, 4F). ^{13}C-NMR-(CD_3OD): $\delta = 163.80$ (q, $J_{C–B} = 49.9$ Hz, arom. C-1), 139.15 (s, arom. C-6), 133.71 (d, $J = 8.8$ Hz, arom. C-2), 127.02 (d, $J = 2.9$ Hz, arom. C-5), 124.61 (dsept, $J = 2.9$ and 16.6 Hz, arom. C-3), 122.13 (dq, $J = 29.4$ and 285.6 Hz, CF_3), 120.52 (d, $J = 10.8$ Hz, arom. C-4), 93.52 (dsept, $J = 32.3$ and 198.6 Hz, $CF(CF_3)_2$), and 55.76 ppm (t, $J_{C–N} = 3.9$ Hz, $N(CH_3)_4$). Anal. Found: C, 44.86; H, 2.69; N, 1.57%. Calcd. for $C_{40}H_{28}NBF_{28}$: C, 45.09; H, 2.65; N, 1.31%.

*3.4.5. Tetramethylammonium tetrakis(3-(trifluoromethyl)-phenyl)borate (**14**)*

The Grignard reagent, which was prepared from 3-(trifluoromethyl)bromobenzene (4.26 g, 17.8 mmol) and magnesium (0.52 g, 21.4 mmol) in the presence of butylmagnesium bromide prepared in situ by the addition of butyl bromide (26 mg, 0.2 mmol), was reacted with boron trifluoride etherate (537 mg, 3.8 mmol). The reaction mixture was heated under reflux for 21 h, and then worked up as above to yield colorless crystals of tetramethylammonium tetrakis(3-(trifluoromethyl)phenyl)borate (**14**) (600 mg, 24% yield) melting at 167–168°C (from dichloromethane-hexane). ^{1}H-NMR (CD_3CN): $\delta = 7.6$–7.0 (br, arom., 16H) and 3.02 ppm (s, $N(CH_3)_4$, 12H). ^{19}F-NMR (CD_3CN): $\delta = 101.87$ ppm (s, CF_3). ^{13}C-NMR(CD_3CN): $\delta = 163.30$ (q, $J_{C–B} = 49.9$ Hz, arom. C-1), 140.14 (s, arom. C-6), 131.91 (s, arom. C-2), 128.44 (q, $J = 30.0$ Hz, arom. C-3), 127.49 (q, $J = 2.9$ Hz, arom. C-5), 126.59 (q, $J = 271.4$ Hz, CF_3), 120.54 (d, $J = 4.9$ Hz, arom. C-4), and 56.14 ppm (t, $J_{C–N} = 3.9$ Hz, $N(CH_3)_4$). Anal. Found: C, 57.85; H, 4.23; N, 2.11%. Calcd. for $C_{32}H_{28}NBF_{12}$: C, 57.76; H, 4.24; N, 2.11%.

Table 5
Molar extinction coefficients at absorption maximum

Borate	Substituent		ε (λ max/nm)
	R^1	R^2	
2	$(CF_2)_3CF_3$	$(CF_2)_3CF_3$	5889 (272)
PFPB(3)	$CF(CF_3)_2$	$CF(CF_3)_2$	4942 (270)
4	CF_3	$CF(CF_3)_2$	4775 (270)
5	H	$CF(CF_3)_2$	4796 (270)
14	H	CF_3	5214 (270)

3.5. Measurements of solubilities of tetraarylborates

A relationship between concentration and absorbance at a keyband was determined with dichloromethane solutions of a range of known concentrations of each tetraarylborate. Molar extinction coefficients in dichloromethane were calculated from the slopes of these linear plots as summarized in Table 5. Solubilities were determined by the photometric method in a similar manner as previously described [9].

3.6. Measurements of decomposition rates of tetraarylborates

3.6.1. Decomposition under dichloromethane/aqueous sulfuric acid two-phase conditions

Aqueous sulfuric acid (2 ml) of prescribed concentration was added into a 2 ml portion of the dichloromethane solution of tetraarylborate (3.87×10^{-3} mol dm^{-3} borate) with vigorously stirring by rotating paddles at 1100 rpm on a water bath thermostatted at 27.0°C. Aliquots were taken from the dichloromethane layer at regular intervals, and quenched immediately with aqueous sodium carbonate. Formation of acid-catalyzed decomposition product, i.e., polyfluoroalkyl-substituted benzene, was traced by monitoring the increase in a gas-chromatographic peak intensity relative to that of decane which was added in advance into the reaction mixture as an internal standard. Pseudo-first-order rate constants, k_1' (Table 3), were calculated from the gradient at the initial stage of rate plots which were linear with the correlation coefficients of more than 0.99 in each reaction system through the decompostion of two-thirds of the initial charge.

3.6.2. Decomposition in methanolic sulfuric acid

Into a precisely weighed amount of tetraarylborate salt (ca. 20 mg) placed in an NMR-sample tube was added methanolic sulfuric acid up to 25 mm high. The sum total of ^{19}F-NMR signal intensities and the decrease in the intensity of CF_3 signals due to the tetraarylborate were traced at 25°C at regular intervals. Pseudo-first-order rate constants (Table 4) were calculated from the rate plots which were linear with the correlation coefficients of more than 0.999 through three half-life periods in each reaction system except **PFPB** (**3**). Decomposition of the last borate (**4**) was traced for 4500 min up to 20% decrease, which followed a pseudo-first-order rate plot with the correlation coefficient of more than 0.999.

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