Syntheses and lipophilicities of tetraarylborate ions substituted with many trifluoromethyl groups

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Abstract

Syntheses were investigated using various tetraarylborate ions with a large number of trifluoromethyl groups: tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, tetrakis [3,5-bis(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)phenyl]borate; tetrakis[3-(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl)phenyl] borate, and tetrakis[3-(2,2,2-trifluoro-1-(2,2,2-trifluoroethyoxy)-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl)phenyl]borate ions. The preparation of Grignard reagents and the subsequent reaction with boron trifluoride etherate are important steps for a higher yield and easier isolation of the product. Sodium- and tetramethylammonium salts of these borate ions are soluble in halocarbon solvents such as dichloromethane, chloroform and 1,2-dibromotetrafluoroethane.

Introduction

We have explored the synthesis of highly lipophilic and bulky but stable anions which are capable of incorporating various cations into hydrophobic solution phases in the form of ion pairs. Previously, we have demonstrated such a species with the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ion (**1**; TFPB). The introduction of trifluoromethyl groups into the 3- and 5-positions on each phenyl group of the parent tetraphenylborate (**2**; TPB) skeleton resulted in a remarkable increase in the solubility of the borate salt in hydrophobic organic solvents and, at the same time, improved the chemical stability under acid and oxidative conditions [1].

Structural features of TFPB (**1**) are summarized as follows: (i) the negative charge is localized on the boron atom at the symmetric center; (ii) the charged center is tightly shielded by four trifluoromethyl-substituted phenyl groups, so as to be separated far from the counter cation;

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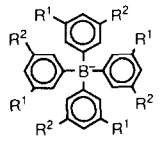
(iii) the charged boron atom is coordinately saturated, and cannot be covalently bonded with the counter cation; (iv) lipophilic trifluoromethyl groups are arrayed to cover the molecular surface, so that the bulky anion is highly hydrophobic. In these respects the structure of TFPB (**1**) is very different from those of ordinary organic anions of a conjugate-base type.

Cations paired with TFPB (**1**) in a hydrophobic solution phase are of interest since they are slightly or non-solvated, almost 'naked', and expected to be highly electrophilic. Thus, the TFPB ion (**1**) was successfully applied as the first effective catalyst [2] in anionic phase-transfer catalysis (PTC) reactions. TFPB (**1**) was found to incorporate various cationic species such as arenediazonium ions, oxonium ions and 1,1'-dimethyl-4,4'-bipyridinium ion (methylviologen) in the form of an ion pair from an aqueous phase into dichloromethane and promote electrophilic reactions of the cationic species under PTC conditions such as diazo-coupling [3], Friedel- Crafts alkylation [4] and electron-transfer reactions [5] Remarkable properties of TFPB (**1**) and the tetrakis[3,5-bis(1-methoxy-2,2-2-trifluoro-1-(trifluoromethyl)ethyl)phenyl]borate ion (**3**) are further demonstrated in their applications as highly lipophilic ion-exchangers for a vitamin B_1-sensitive liquid-membrane electrode [6] and as a novel electron-donor in photo-induced electrochromism of charge-transfer complexes of TFPB (**1**) paired with methylviologen and its homologues [7].



(1) TFPB $R^1 = R^2 = CF_3$
(2) TPB $R^1 = R^2 = H$
(3) $R^1 = R^2 = C(CF_3)_2OCH_3$
(4) $R^1 = CF_3$, $R^2 = C(CF_3)_2OCH_3$
(5) $R^1 = CF_3$, $R^2 = C(CF_3)_2OCH_2CF_3$
(6) $R^1 = R^2 = C(CF_3)_2OCH_2CF_3$

Fig 1 Tetraarylborates

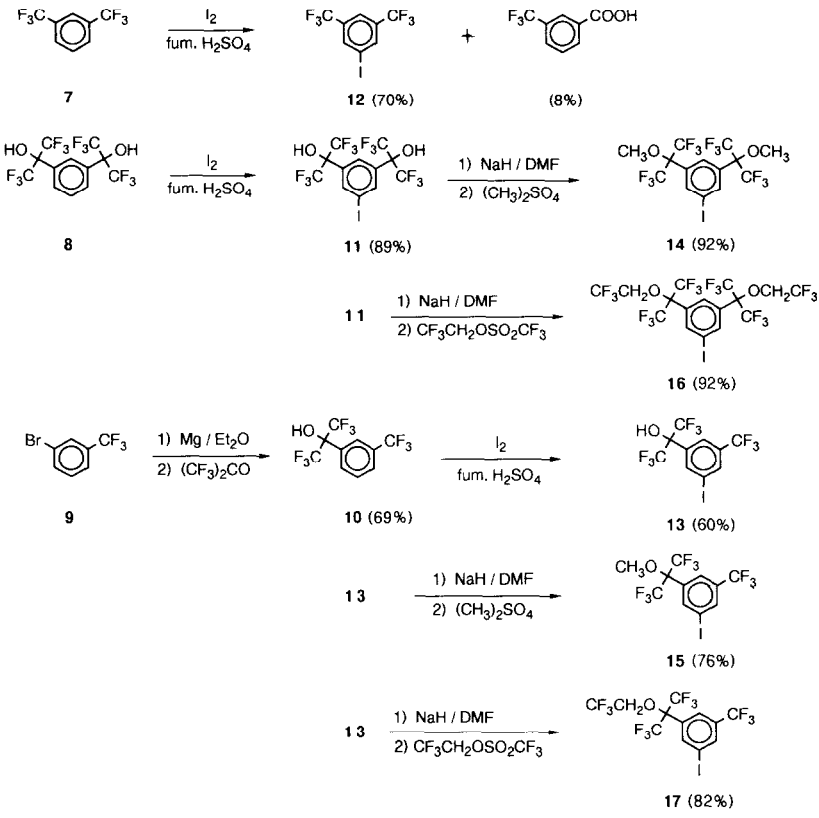
These results stimulated us to explore homologous anions containing a larger number of trifluoromethyl groups, which should be more soluble in hydrophobic organic solvents than TFPB (**1**).

In this paper, we report the syntheses and the lipophilicities of several kinds of tetraphenylborate homologues with a large number of trifluoromethyl groups on each phenyl group· the borate **3**, tetrakis-[3-(1-methoxy - 2,2,2 - trifluoro - 1 - (trifluoromethyl)ethyl) - 5 - (trifluoromethyl)phenyl]borate ion (**4**), and tetrakis[3-(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy) - 1 - (trifluoromethyl)ethyl) - 5 - (trifluoromethyl)phenyl]borate ion (**5**). An improved preparation of TFPB (**1**) is also described. Attempts to synthesize tetrakis[3,5-bis(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl)phenyl]borate ion (**6**) have so far been unsuccessful.

Results and discussion

Preparation of intermediates for the borate syntheses (Scheme 1)

The starting intermediates **7**, **8** and **9** were chosen from commercially available reagents. Introduction of the 1-hydroxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl group into the aromatic ring of **9** was achieved by bubbling hexafluoroacetone into an ethereal Grignard reagent from **9**, to give **10** (69% yield).



Scheme 1.

Direct iodination of 7, 8 and 10

Introduction of an iodo-substituent onto an aromatic ring having trifluoromethyl groups, such as in compound **7**, has previously been carried out by a laborious multi-step process: nitration, reduction to amine, diazotization and iodination (34% overall yield [8]). A one-step iodination of **7** and **10** in a similar manner to that of **8** to give the iodide **11** [9] afforded good yields of the corresponding iodides **12** and **13** (70% and 60% yields, respectively) using iodine in 30% fuming sulfuric acid at

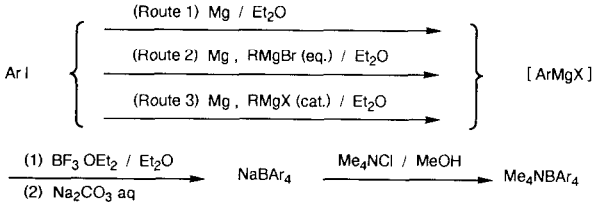
room temperature. In the iodination of **7**, partially hydrolyzed 3-trifluoromethylbenzoic acid was isolated as a by-product (8% yield). In the preparation of the iodobenzene derivatives **14** to **17** (see below) containing ether bonds on their side chains, the benzene ring had to be iodinated prior to the etherification, since the resulting ether bond was labile under the acid iodination conditions.

Etherification of the hydroxyl group on the side chain

The hydroxyl groups on the side chain of the iodides **11** and **13** were converted to methoxyl groups to give the iodo-ethers **14** and **15** (92% and 76% yields, respectively), by treatment with sodium hydride and subsequently dimethyl sulfate in DMF. Similar treatment with sodium hydride and 2,2,2-trifluoroethyl trifluoromethanesulfonate converted the iodides **11** and **13** to the corresponding 2,2,2-trifluoroethoxyl derivatives **16** and **17** (92% and 82% yields, respectively).

Grignard reaction to form tetraarylborates, TFPB (1) and borates 3, 4, 5 and 6

Tetraarylborates were prepared by the reactions of Grignard reagents derived by several methods from aryl iodides with 1/5 to 1/6 molar amounts of boron trifluoride etherate ($BF_3 \cdot OEt_2$), as shown in Scheme 2.



Scheme 2.

Preparation of TFPB (1)

Metal–halogen exchange reaction for the preparation of the Grignard reagent afforded a satisfactory yield of TFPB (**1**) and, moreover, easier isolation than the previous method [1] in obtaining crystalline sodium- or tetramethylammonium salts. When a Grignard reagent was prepared directly from the iodide **12** and an equi-gram atom of magnesium in ether (Route 1 in Scheme 2), followed by the subsequent reaction with 1/5 equimolar amount of $BF_3 \cdot OEt_2$ and the resulting mixture was worked up with saturated aqueous sodium carbonate, the sodium salt of TFPB (**1**) was formed in a satisfactory yield (78% based on $BF_3 \cdot OEt_2$). However, repeated laborious chromatographic separations were necessary to isolate a crystalline salt from the product mixture in high yield. On the other hand, when the Grignard reagent was prepared by a metal–halogen exchange reaction of the iodide **12** with an equimolar amount of octylmag-

nesium bromide (Route 2 in Scheme 2), the subsequent reaction with a 1/10 equimolar amount of $BF_3 OEt_2$ afforded sodium TFPB (**1**) in an isolated yield of 66%; this seemed low in comparison with the above value of 78%, but the sodium salt was easily obtained as a crystalline precipitate simply by supersonic irradiation of the product mixture in hexane. In a similar manner, reaction of the iodide **12** with an equimolar amount of ethylmagnesium bromide and 1/6 equimolar $BF_3 OEt_2$ gave sodium TFPB (**1**) (49% yield).

Tetramethylammonium TFPB (**1**) was obtained by treating the sodium salt with an excess of tetramethylammonium chloride in methanol, while ion-exchange for other alkali metal ions was achieved by equilibration between an aqueous alkali metal chloride and ethereal sodium TFPB (**1**).

Tetrakis[3,5-bis(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)phenyl]borate (3)

The preparation of a Grignard reagent for the borate **3** derived from the iodide **14** and magnesium seemed more difficult to control, compared with that for TFPB (**1**) from the iodide **12**; the yields of borate **3** differed from one batch to another, as shown in Table 1. Direct reaction of the iodide **14** with magnesium to give the Grignard reagent without the addition of any initiating catalyst, followed by treatment with $BF_3 \cdot OEt_2$, resulted in only a 22% isolated yield of the sodium salt (Entry 1). When a Grignard reaction of the iodide **14** with 1.1 equi-gram atom of magnesium was initiated by the addition of 3 mol% of the same Grignard reagent prepared separately from the iodide **14** and magnesium (Route 3 in Scheme 2), and followed by treatment with $BF_3 \cdot OEt_2$, then the tetramethylammonium salt of the borate **3** was isolated in a somewhat increased yield (40%) (Entry 2). On the other hand, a similar reaction of the iodide **14** with an equi-gram atom of magnesium, in the presence of 2 mol% of the same Grignard reagent (prepared separately by metal–halogen exchange of the iodide **14** with an equimolar amount of octylmagnesium bromide) and subsequent treatment with $BF_3 \cdot OEt_2$ gave the sodium salt (91% yield) as the tetrahydrate (Entry 3).

Detailed investigation of the conditions for the reaction indicated that a larger amount of residual magnesium metal remaining in the Grignard reagent solution caused the subsequent reaction with $BF_3 \cdot OEt_2$ to be more complex and, consequently, isolation of crystalline sodium- and tetramethylammonium salts of the borate **3** was more difficult. A small-scale reaction of the iodide **14** with an equi-gram atom of magnesium, in the presence of 10 mol% of octylmagnesium bromide, afforded a high yield (83%) of the borate **3** (Entry 4), while a similar but large-scale reaction resulted in a lowered yield (32% of combined crops) (Entry 5). A similar reaction of the iodide **14** in the presence of a different initiating catalyst (butylmagnesium bromide) gave a reasonable yield (59% of combined crops) (Entry 6), while a similar-scale reaction of **14** using a

TABLE 1

Conditions and yields for syntheses of the borate **3**

Entry	ArI(**14**) (mmol)	Catalyst (mol%)	Mg (eq.)	$BF_3 \cdot OEt_2$[a] (eq.)[c]	Refluxing time	Yield[b] of **3**(%) (Counter cation)
1	3.56		1.1	1/4.8	2 d	22[d] (Na)
2	7.66	ArMgI (3)	1.1	1/4.9	3 d	40 (Me_4N)
3	12.7	ArMgBr[e] (2)	1.0	1/5.5	1.5 d	91[d] (Na)
4	3.20	OcBr[f] (10)	1.0	1/4.8	17 h	83 (Me_4N)
5	103	OcBr (10)	1.0	1/5.2	1 d	18 (Na), 14 (Me_4N)
6	102	BuBr[g]	1.0	1/5.2	4 d	27 (Na), 32 (Me_4N)
7	92.6	BuBr (5)	1.1	1/5.0	6 d	not isolated
8	26.0	BuBr (1)	1.0	1/4.6[h]	20 h	5(K), 46 (Me_4N)
9				1/4.5[h]	20 h	59(K)
10				1/5.5[h]	20 h	not isolated
11	88.1	BuBr (1)	1.0	1/4.7	1.5 d	53 (Na)[i], 34 (Me_4N)[i]

[a] $BF_3 \cdot OEt_2$ was added to the Grignard reagent except for entries 9 and 11, where the Grignard reagent was added dropwise into ethereal $BF_3 \cdot OEt_2$.

[b] Yield after recrystallization. Product **3** was isolated as the sodium or potassium salt by precipitation. A portion remaining in the mother liquor was cation-exchanged to the tetramethylammonium salt for easier isolation by precipitation. The latter salt was also purified by recrystallization.

[c] Equivalent based on the aryl iodide **14** used, unless otherwise described.

[d] Apparent yield based on separated solid of sodium salt before recrystallization.

[e] Prepared by metal–halogen exchange reaction of the iodide **14** with equimolar octylmagnesium bromide in ether.

[f] 1-Octyl bromide.

[g] 1-Butyl bromide.

[h] Equivalent based on the arylmagnesium iodide (79% yield) determined by iodination of the Grignard reagent.

[i] Solid sodium and tetramethylammonium salts were separated before recrystallization in 56% and 37% apparent yields, respectively.

small excess (*e.g.* 1.1 equi-gram atom of magnesium) gave no isolable yield (Entry 7).

The results of comparative experiments using portions from the same Grignard reagent were informative. When ethereal $BF_3 \cdot OEt_2$ was added to the first supernatant portion of the Grignard reagent (which was prepared from the iodide **14** and 1.0 equi-gram atom of magnesium in the presence of 1 mol% of butylmagnesium bromide), then the first crop was isolated in the form of the potassium salt (5% yield) and the remainder in the form of the more crystallizable tetramethylammonium salt (46% yield) (Entry 8). When the second supernatant portion of the above Grignard reagent was added to ethereal $BF_3 \cdot OEt_2$, then an increased yield (59%) of the potassium salt of the borate **3** was obtained (Entry 9). On the other hand, when the last portion of the Grignard reagent containing a certain amount of unreacted magnesium was treated similarly with ethereal $BF_3 \cdot OEt_2$, then the product mixture was too complicated to afford a

definite solid borate (Entry 10). These results indicate that removal of unreacted magnesium from the Grignard reagent solution prior to reaction with $BF_3 \cdot OEt_2$ is necessary for high isolated yields of crystalline salts of the borate **3**. When a Grignard reagent solution (which was prepared from the iodide **14** with an equi-gram atom of magnesium in the presence of 1 mol% of butylmagnesium bromide with subsequent separation of residual magnesium) was added dropwise into ethereal $BF_3 \cdot OEt_2$, then an 87% yields of the combined crystalline solids of the sodium- and tetramethylammonium salts of the borate **3** was attained (Entry 11).

Tetrakis[3-(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl)phenyl]borate (4)

The borate **4** was isolated as the tetramethylammonium salt (59% yield) in a direct Grignard reaction of the iodide **15** with 1.1 equi-gram atom of magnesium and subsequent reaction with a 1/6 equimolar amount of $BF_3 \cdot OEt_2$.

Tetrakis[3-(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl)phenyl]borate (5)

In a similar manner, the borate **5** was isolated as the tetramethylammonium salt (30% yield) in a Grignard reaction of the iodide **17** with 1.34 equi-gram atom of magnesium in the presence of 10 mol% of octylmagnesium bromide and with a 1/7.8 equimolar amount of BF_3 OEt_2. Lower isolated yields of the borates **4** and **5** seemed to be caused by the use of an excess amount of magnesium.

Attempts to synthesize tetrakis[3,5-bis(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl)phenyl]borate (**6**)

All attempts to isolate a definite solid product of the borate **6** resulted in failure under reaction conditions in which satisfactory results were afforded in the preparation of the other borates described above.

Lipophilicity of the tetraarylborate derivatives

A remarkable effect of trifluoromethyl groups has been demonstrated in the extraordinarily high partition coefficients of various alkali metal salts of TFPB (**1**) in a dichloromethane–water two-phase system [1]. Since the introduction of a trifluoromethyl group into a TPB skeleton at one of the *meta*-positions of each phenyl group caused only a slight increase in the partition coefficient, we presumed that not only the larger number of trifluoromethyl groups but also the bulkiness of the tetraarylborate ion as a whole are important for the higher lipophilicity.

In order to investigate the relationship between the lipophilicity of tetraarylborate salts and their *meta*-substituents containing different numbers of trifluoromethyl groups, we measured the solubilities of sodium- and tetramethylammonium salts of the tetraarylborates **1**, **3**, **4** and **5** in three kinds of halocarbon solvents (dichloromethane, chloroform and 1,2-dibromotetrafluoroethane) at 25 °C (Table 2).

TABLE 2

Solubilities of tetramethylammonium tetraarylborates in halocarbon solvents at 25.0 °C (mol l^{-1})

Borate compd.	Solvent (Dielectric const.)		
	CH_2Cl_2 (8.93)	$CHCl_3$ (4.81)	$(CBrF_2)_2$ (2.34)
TFPB (1); $R_1 = R_2 = CF_3$	2.0×10^{-2}	1.4×10^{-4}	$< 1.4 \times 10^{-5}$
	7.5×10^{-3}[a]		$< 1.6 \times 10^{-5}$[a]
3; $R_1 = R_2 = C(CF_3)_2OCH_3$	2.2×10^{-1}	3.6×10^{-3}	4.5×10^{-4}
	8.6×10^{-3}[a]		1.3×10^{-4}[a]
4; $R_1 = C(CF_3)_2OCH_3$, $R_2 = CF_3$	7.7×10^{-2}	3.1×10^{-3}	2.2×10^{-4}
5; $R_1 = C(CF_3)_2OCH_2CF_3$, $R_2 = CF_3$	4.0×10^{-3}	1.8×10^{-5}	1.4×10^{-3}

[a]Solubility of sodium salt.

Tetramethylammonium salts were found to be more soluble than the sodium salts. The borates were, in general, more soluble in the more dielectric solvents, except for the tetramethylammonium salt of the borate **5**, whose solubilities in chloroform and in 1,2-dibromotetrafluoroethane were found to be contrary to the general tendency. In polychloromethane solvents such as dichloromethane and chloroform, the order of the ability of the substituents to increase solubility was:

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

This means that the number of trifluoromethyl groups and the overall bulkiness of the substituents are not proportional to the solubilities in these solvents.

On the other hand, the order in 1,2-dibromotetrafluoroethane was:

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

Although no solubility data have been provided for the borate **6**, which has two $C(CF_3)_2OCH_2CF_3$ groups on the *meta*-positions of each phenyl, nor those of the borates **1**, **3**, **4** and **5** in other polyfluorocarbon solvents, it is reasonable to assume that the larger number of trifluoromethyl groups covering the surface of the borate ion cause an increase in solubility of the borate ion in polyfluorocarbon solvents such as 1,2-dibromotetrafluoroethane.*

Further studies are underway to synthesize tetraarylborate ions with a larger number of perfluoroalkyl groups which are stable and soluble in polyfluorocarbon solvents.

*A similar solubility order was observed in our studies on tetraarylborate salts with perfluoroalkyl substituents on the *meta*-positions of each phenyl group.

Experimental

NMR spectra were obtained on a JEOL FX-100 spectrometer at 99.6 MHz for ^1H and at 93.65 MHz for ^{19}F, and on a JEOL-GSI 270 at 270 MHz for ^1H and at 67.94 MHz for ^{13}C as proton wide-band decoupled spectra in a deuterochloroform solution with TMS and hexafluorobenzene as internal references, unless otherwise described. Mass spectra were recorded on a JEOL-JMS-01SG-2 instrument. 1,3-Bis(trifluoromethyl)benzene (**7**) and 3-(trifluoromethyl)bromobenzene (**9**) were commercially available reagents. 1,3-Bis[1-hydroxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-benzene (**8**) was provided by Central Glass Co. All the starting compounds were used after purification by appropriate methods.

*1-[1-Hydroxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-3-(trifluoromethyl)benzene (**10**)*

Into a Grignard reagent solution prepared from 3-(trifluoromethyl)bromobenzene (**9**) (20.00 g, 88.9 mmol) and magnesium turnings (2.20 g, 90.5 mmol) in dry diethyl ether (25 ml), gaseous hexafluoroacetone was bubbled until no more Grignard reagent remained (*ca.* 4 h). Usual work-up of the reaction mixture yielded a colorless oil (19.16 g, 69% yield), b.p. 62.5 °C/15 Torr. ^1H NMR: $\delta = 8.0–7.5$ (m, arom. 4H) and 3.90 ppm (s, OH, 1H). ^{19}F NMR: $\delta = 99.0$ (s, Ar–CF_3, 3F) and 86.2 ppm (s, $C(CF_3)_2OH$, 6F). MS: m/z (rel. intensity) = 312(M^+, 28), 293(20), 243(74), 173(100), 145(41), 127(28), 91(26), 69(25) and 43(40).

Direct iodination procedure (typical procedure)

*3,5-Bis(trifluoromethyl)iodobenzene (**12**)*

Into a dark solution of iodine (42.67 g, 0.17 mol) in 30% fuming sulfuric acid (110 ml) was added dropwise 1,3-bis(trifluoromethyl)benzene (**7**) (30.05 g, 0.14 mol) over 2 h with vigorous stirring. The resultant mixture was stirred for an additional 7 h at room temperature, and then poured portion-wise into crushed ice (600 g). The separated dark oil was extracted with ether six times (100 ml each), 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 magnesium sulfate and evaporated to give an oily residue, which was fractionated under reduced pressure to afford a colorless oil of the iodide **12**, b.p. 58.2 to 59.0 °C/11 Torr (lit. [8], b.p. 59 to 61 °C/10 Torr) (33.56 g, 70% yield).

From the distillation residue, colorless crystallites were isolated and identified as 3-(trifluoromethyl)benzoic acid (2.26 g, 8% yield), colorless needles, m.p. 105 °C (from hexane) (lit. [10], m.p. 103 to 104.5 °C). ^1H NMR: $\delta = 8.5–7.5$ (m, arom., 4H) and 10.2 ppm (br s, COOH, 1H); ^{19}F NMR: $\delta = 98.7$ ppm (s, CF_3); MS: $m/z = 190(M^+)$.

When the reaction of **7** (10.00 g, 46.7 mmol) with iodine (11.90 g, 46.7 mmol) was carried out in a similar manner (except that an elevated

temperature such as 55 °C was used), the yield of the iodide **12** was reduced to 52% (8.23 g), accompanied by the formation of 3-iodo-5-(trifluoromethyl)benzoic acid (2.61 g, 18% yield) as a by-product, as colorless needles, m.p. 140 °C (from hexane). ^{1}H NMR: $\delta = 8.62$ (s, arom., 1H), 8.33 (s, arom., 1H), 8.19 (s, arom., 1H) and 4.7 ppm (br s, COOH, 1H); ^{19}F NMR: $\delta = 99$ ppm (s, CF_3);* MS: m/z (rel. intensity) = 316 (M^+, 7), 144(40), 127(100), 75(48), 74(47) and 46(41).

3,5-Bis[1-hydroxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]iodobenzene (11)

By use of the starting compound **8** (48.46 g, 0.118 mol) and iodine (36.28 g, 0.143 mol), the corresponding iodide **11** was isolated (56.08 g, 89% yield; GLC purity 98%) as a colorless oil, b.p. 73.5 to 75 °C/0.6 Torr (lit. [9], b.p. 80 °C/0.1 Torr). ^{1}H NMR: $\delta = 8.18$ (s, arom., 2H), 8.07 (s, arom., 1H) and 3.56 ppm (s, OH, 2H); ^{19}F NMR: $\delta = 86.2$ ppm (s, CF_3), ^{13}C NMR: $\delta = 138.0$ (s, arom. C-2,6), 132.1 (s, arom. C-3,5), 124.8 (s, arom. C-4), 122.6 (q, $J = 287$ Hz, CF_3), 94.4 (s, arom. C-1), and 76.4 ppm (q-like m, $J = 30$ Hz, $C(CF_3)_2OH$); MS: accurate m/z (found) = 535.914; calcd. for $C_{12}H_5O_2F_{12}I$, $m/z = 535.9144$.

3-[1-Hydroxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-5-(trifluoromethyl)iodobenzene (13)

By use of the starting compound **10** (15.63 g, 50.0 mmol) and iodine (15.45 g, 60.9 mmol) the corresponding iodide **13** was isolated (13.03 g, 60% yield) as a colorless oil, b.p. 71.5 °C/4 Torr. ^{1}H NMR: $\delta = 8.19$ (s, arom., 1H), 8.03 (s, arom., 1H) 7.90 (s, arom., 1H) and 2.65 ppm (s, OH, 1H); ^{19}F NMR: $\delta = 99.0$ (s, Ar–CF_3, 3F) and 86.2 ppm (s, $C(CF_3)_2$, 6F); ^{13}C NMR: $\delta = 139.0$ (s, arom. C-2), 136.4 (q, $J = 4$ Hz, arom. C-6), 132.8 (q, $J = 33$ Hz, arom. C-5), 132.2 (s, arom. C-3), 123.1 (s, arom. C-4), 122.5 (q, $J = 274$ Hz, $C(CF_3)_2$), 122.2 (q, $J = 288$ Hz, Ar–CF_3), 94.0 (s, arom. C-1) and 76.4 (sept., $J = 30$ Hz, $C(CF_3)_2OH$); MS: m/z (rel. intensity) = 438(M^+, 100), 369(37), 299(43), 253(16), 144(15) and 69(16); accurate m/z (found) = 437.916; calcd. for $C_{10}H_4OF_9I$, $m/z = 437.9164$.

Etherification procedure

3,5-Bis[1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]iodobenzene (14)

A sodium alkoxide prepared under a nitrogen atmosphere from the diol **11** (20.51 g, 38.3 mmol) in DMF (60 ml) and sodium hydride (60% in oil, 3.19 g, 79.6 mmol as hydride) below 0 °C, was methylated by the slow addition of dimethyl sulfate (9.94 g, 78.8 mmol). The reaction was completed by heating for 15 min at 40 °C. The reaction mixture was poured into ice, acidified with diluted hydrochloric acid, and extracted five times

*Measured on a Hitachi R-24F at 56.4 MHz for ^{19}F.

with ether (100 ml each). Usual work-up of the ethereal extracts afforded an orange-colored crude product, which was fractionated to give the corresponding dimethoxy product **14** (19.88g, 92% yield, GLC purity 91%), b.p. 63 to 65 °C/0.1 Torr (lit. [11], b.p. 126 °C/10 Torr). ^{1}H NMR: $\delta = 8.03$ (s, arom. H-2,6, 2H), 7.80 (s, arom. H-4, 1H) and 3.51 ppm (t, $J = 1$ Hz, OCH_3, 6H); ^{19}F NMR: $\delta = 91.1$ ppm (s, CF_3); ^{13}C NMR: $\delta = 139.0$ (s, arom. C-2,6), 131.0 (s, arom. C-3,5), 127.7 (s, arom. C-4), 122.1 (q, $J = 289$ Hz, CF_3), 94.3 (s, arom. C-1), 82.3 (sept., $J = 29$ Hz, $C(CF_3)_2$ and 54.6 ppm (s, OCH_3); MS: $m/z = 564$ (M^+). Analysis: Found: C, 29.92; H, 1.75%. Calcd. for $C_{14}H_9O_2F_{12}I$: C, 29.81; H, 1.61%.

A minor by-product was identified as 1,3-bis[1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]benzene, m.p. 86.5 to 87.0 °C (lit. [11], m.p. 81 to 84 °C). ^{1}H NMR: $\delta = 7.9$–7.4 (m, arom., 4H) and 3.5 ppm (t, $J = 1$ Hz, OCH_3, 6H); ^{19}F NMR: $\delta = 90.8$ ppm (s, CF_3); ^{13}C NMR: $\delta = 130.2$ (s, arom. C-4,6), 129.4 (s, arom. C-1,3), 129.0 (s, arom. C-5), 128.4 (s, arom. C-2), 122.3 (q, $J = 289$ Hz, CF_3), 82.9 (sept, $J = 28$ Hz, $C(CF_3)_2$), and 54.4 ppm (s, OCH_3); MS: $m/z = 438$ (M^+).

*3,5-Bis[2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl]iodobenzene (**16**)*

The sodium alkoxide prepared under an argon atmosphere from the diol **11** (9.96 g, 18.6 mmol) in DMF (25 ml) and sodium hydride (60% in oil, 1.65 g, 41.3 mmol as hydride) below 0 °C, was trifluoroethylated by the addition, with stirring, of 2,2,2-trifluoroethyl trifluoromethanesulfonate (10.22 g, 44.0 mmol) in one portion. The reaction was completed by heating for 35 min at 50 °C. The reaction mixture was poured into saturated aqueous ammonium chloride, neutralized with diluted hydrochloric acid, and extracted three times with ether (50 ml each). Usual work-up of the ethereal extracts afforded a pale-yellow crude product, which was fractionated to give the corresponding bis(trifluoroethoxyl), product **16** (10.54 g, 92% yield), b.p. 74 to 75 °C/0.2 Torr. ^{1}H NMR: $\delta = 8.06$–7.85 (m, arom., 3H) and 4.0 ppm (q, $J = 7$ Hz, OCH_2CF_3, 4H); ^{19}F NMR: $\delta = 91.2$ (s, $C(CF_3)_2$, 12F) and 87.6 ppm (t, $J = 7$ Hz, OCH_2CF_3, 6F); MS: m/z (rel. intensity) = 701(17), 700(M^+, 100), 681(16), 632(11), 631(63) and 83(28); accurate m/z (found) = 699.921; calcd. for $C_{16}H_7O_2F_{18}I$, $m/z = 699.9204$.

*3-[1-Methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-5-(trifluoromethyl)iodobenzene (**15**)*

The sodium alkoxide derived from the alcohol **13** (11.07 g, 25.3 mmol) in DMF (30 ml) and sodium hydride (60% in oil, 1.10 g, 27.5 mmol as hydride) was methylated with dimethyl sulfate (3.56 g, 28.3 mmol). Usual work-up afforded the corresponding methoxyl product **15** (8.65 g, 76% yield), b.p. 84 °C/7 Torr. ^{1}H NMR: $\delta = 8.10$ (br s, arom., 2H), 7.81 (br s, arom., 1H) and 3.54 ppm (t, $J = 1$ Hz, OCH_3, 3H); ^{19}F NMR: $\delta = 98.8$ (s, Ar–CF_3, 3F) and 91.2 ppm (s, $C(CF_3)_2$, 6F); ^{13}C NMR: $\delta = 140.4$ (s, arom. C-2), 136.5 (q, $J = 3$ Hz, arom. C-6), 133.1 (q, $J = 33$ Hz, arom. C-5), 131.5 (s,

arom. C-3), 124.5 (s, arom. C-4), 122.5 (q, $J = 273$ Hz, $C(CF_3)_2$, 122.0 (q, $J = 289$ Hz, Ar–CF_3), 94.1 (s, arom. C-1), 82.1 (sept., 29 Hz, $C(CF_3)_2$) and 54.8 ppm (s, OCH_3); MS: m/z (rel. intensity) = 453(13), 452(M^+, 100), 433(18), 383(83), 299(27), 187(14), 144(12), and 69(14); accurate m/z (found) = 451.932; calcd. for $C_{11}H_6OF_9I$, $m/z = 451.9321$.

3-[2,2,2-Trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl]-5-(trifluoromethyl)iodobenzene (17)

The sodium alkoxide derived from the alcohol **13** (9.89 g, 22.6 mmol) in DMF (30 ml) and sodium hydride (60% in oil, 1.23 g, 30.8 mmol as hydride) was trifluoroethylated with 2,2,2-trifluoroethyl trifluoromethanesulfonate (6.91 g, 29.9 mmol). Usual work-up afforded the corresponding trifluoroethoxyl product **17** (9.61 g, 82% yield), b.p. 54 to 55 °C/0.9 Torr. ^{1}H NMR: $\delta = 8.15$–7.87 (m, arom., 3H) and 4.02 ppm (q, $J = 8$ Hz, OCH_2, 2H); ^{19}F NMR: $\delta = 98.6$ (s, Ar–CF_3, 3F), 91.2 (s, $C(CF_3)_2OCH_2$, 6F) and 87.5 ppm (t, $J = 8$ Hz, CH_2CF_3, 3F).

Syntheses of tetraarylborates

(A) Typical procedure by metal–halogen exchange; sodium tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate (1; TFPB)

Into ethereal octylmagnesium bromide (which was prepared from 1-bromooctane (0.98 g, 5.1 mmol) and magnesium (0.15 g, 6.2 mmol) in diethyl ether (5 ml) under an argon atmosphere), was added dropwise over 5 min ethereal 3,5-bis(trifluoromethyl)iodobenzene (**12**) (1.67 g, 4.93 mmol in 1 ml of diethyl ether), and subsequently ethereal boron trifluoride (2.72 g of a solution containing 72.5 mg of $BF_3{\cdot}OEt_2$, 1/9.7 eq. based on iodide **12**), over 5 min, with stirring and cooling on an ice bath. The reaction mixture was heated under reflux for an additional 19 h, and then quenched by the addition of saturated aqueous sodium hydrogen carbonate (20 ml). Precipitates were removed by filtration, and an aqueous layer of the filtrate was extracted repeatedly with diethyl ether. The ethereal layer and extracts were combined and worked-up as usual. The crude product was sonicated in hexane, and the precipitated sodium salt of **1** (0.32 g, 66% yield based on $BF_3{\cdot}OEt_2$) was recrystallized from chloroform and identified by spectral comparisons with the authentic specimen [1].

Tetramethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1)

The sodium salt of the borate **1** dissolved in methanol was sonicated after the addition of an excess amount of methanolic tetramethylammonium chloride, and then the solvent was evaporated off. The residue was dispersed in water and the mixture was extracted repeatedly with diethyl ether. The extracts were combined and evaporated off, and then the solid residue was recrystallized from a dichloromethane–hexane mixture, to yield the colorless tetramethylammonium salt of TFPB (**1**), m.p. 258 to 260 °C. ^{1}H NMR ($CDCl_3$–CD_3CN): $\delta = 7.70$ (br s, arom., 8H), 7.56 (br s, arom., 4H) and 3.06 (d, $J = 0.5$ Hz, $N(CH_3)_4$, 12H); ^{19}F NMR ($CDCl_3$–

CD_3CN): $\delta = 99.7$ ppm (s, CF_3), ^{13}C NMR ($CDCl_3$–CD_3CN): $\delta = 161.8$ (q, J(C–B) = 50 Hz, arom. C-1), 134.9 (s, arom. C-2,6), 129.1 (qq, $J = 31$ and 3 Hz, arom. C-3,5), 124.7 (q, $J = 272$ Hz, CF_3), 117.7 (t-like m, $J = 4$ Hz, arom. C-4) and 55.8 ppm (t, J(C–N) = 4 Hz, NCH_3). Analysis Found: C, 46.21; H, 2.71; N, 1.40%. Calcd. for $C_{36}H_{24}NBF_{24}$: C, 46.12; H, 2.59; N, 1.49%.

(B) Typical procedure using an initiating catalyst: Tetramethylammonium tetrakis[3,5-bis(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)phenyl]borate (3) (entry 11 in Table 1)

Step (1), preparation of Grignard reagent: 1-Bromobutane (137 mg, 1.00 mmol) was added to diethyl ether (12 ml) containing magnesium (2.14 g, 88.1 mmol) under an argon atmosphere, to form butylmagnesium bromide. To the resulting mixture containing butylmagnesium bromide and magnesium was added an ethereal solution (100 ml) of 3,5-bis[1-methoxyl-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]iodobenzene (**14**) (48.71 g, 88.1 mmol) and maintained for 45 min at 0 °C to generate the corresponding Grignard reagent; the mixture was then stirred for an additional 4 h at room temperature to complete the reaction.

Step (2), Grignard reaction. A supernatant solution of the Grignard reagent was added dropwise to boron trifluoride etherate (2.67 g, 18.8 mmol, 1/4.7 eq.) in diethyl ether (20 ml) for 10 min at 0 °C, and the reaction mixture was heated under reflux for an additional 1.5 days. After the usual work-up, a crude product was sonicated in dichloromethane–hexane to afford solid precipitates of the sodium salt of **3** (19.50 g, 56% yield). A remaining portion dissolved in the mother liquor was cation-exchanged by treating with an excess of tetramethylammonium chloride in a similar manner as above, and the resulting solid precipitates were sonicated in dichloromethane–hexane to isolate the tetramethylammonium salt of **3** (12.66 g, 37% yield). The sodium- and tetramethylammonium salts were purified by recrystallization from a dichloromethane–hexane mixture (53% and 34%, respectively); both melted with decomposition at temperatures higher than 300 °C. Sodium salt: ^1H NMR ($CDCl_3$–CD_3CN): $\delta = 7.48$ (br s, arom., 8H), 7.35 (s, arom., 4H), 3.25 (s, OCH_3, 24H) and 2.13 ppm (s, H_2O); ^{19}F NMR ($CDCl_3$–CD_3CN): $\delta = 90.8$ ppm (s, CF_3); ^{13}C NMR ($CDCl_3$–CD_3CN): $\delta = 162.1$ (q, J(C–B) = 50 Hz, arom. C-1), 137.0 (s, arom. C-2,6), 125.3 (s, arom. C-3,5), 123.0 (s, arom. C-4), 122.6 (q, J(C–F) = 290 Hz, CF_3), 83.2 (sept, ^2J(C–F) = 28 Hz, $C(CF_3)_2$) and 53.6 ppm (s, OCH_3). Analysis: Found: C, 36.34; H, 2.34%. Calcd. for $C_{56}H_{36}O_8BF_{48}Na{\cdot}4H_2O$: C, 36.27; H, 2.39%. Tetramethylammonium salt: $\lambda_{max}(\varepsilon)$ (CH_2Cl_2): 283 (5.5×10^3) and 273 nm (5.5×10^3); ^1H NMR ($CDCl_3$–CD_3CN): $\delta = 7.42$ (br s, arom., 8H), 7.32 (s, arom., 4H), 3.24 (s, OCH_3, 24H) and 3.12 ppm (d, $J = 12$ Hz, $N(CH_3)_4$, 12H). ^{19}F NMR ($CDCl_3$–CD_3CN): $\delta = 90.8$ ppm (s, CF_3). Analysis: Found: C, 38.90; H, 2.64; N, 0.61%. Calcd. for $C_{60}H_{48}NO_8BF_{48}{\cdot}H_2O$: C, 38.91; H, 2.73; N, 0.76%.

Tetramethylammonium tetrakis[3-(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl)phenyl]borate (4)

A Grignard reagent [which was prepared from 3-[1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-5-(trifluoromethyl)iodobenzene (**15**) (2.30 g, 5.09 mmol) and magnesium (0.136 g, 5.60 mmol)] was reacted *in situ* with boron trifluoroiride etherate (120 mg, 0.85 mmol) in dry diethyl ether (6 ml). The reaction mixture was heated under reflux for 24 h, and then worked-up in a similar manner as above to yield a pale-yellow solid of the crude sodium salt of the borate **4** (0.92 g, 81% yield). The methanolic sodium salt of the borate **4** was ion-exchanged with an excess of tetramethylammonium chloride to afford colorless crystals of the corresponding tetramethylammonium salt, which decomposed at 141 °C (from dichloromethane–hexane). ^{1}H NMR ($CDCl_3$–DMSO-d_6): δ = 7.67–7.33 (m, arom., 12H), 3.20 (s, OCH_3, 12H) and 3.01 ppm (s, $N(CH_3)_4$, 12H); ^{19}F NMR ($CDCl_3$–DMSO-d_6): δ = 99.8 (s, Ar–CF_3, 12F) and 90.8 ppm (s, $C(CF_3)_2OCH_3$, 24F), $\lambda_{max}(\varepsilon)$ (CH_2Cl_2): 280 (4.5×10^3) and 272 nm (5.2×10^3) Analysis: Found: C, 41.43; H, 2.69; N, 1.26%. Calcd. for $C_{48}H_{36}NO_4BF_{36}$: C, 41.61; H, 2.62; N, 1.01%.

Tetramethylammonium tetrakis[3-(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl)phenyl]borate (5)

A Grignard reagent [which was prepared from 3-[2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl]-5-(trifluoromethyl)iodobenzene (**17**) (3.00 g, 5.77 mmol) and magnesium (0.16 g, 6.58 mmol) in the presence of octylmagnesium bromide (0.11 g, 0.57 mmol)] was reacted *in situ* with boron trifluoride etherate (160 mg, 1.13 mmol) in dry diethyl ether (7 ml). The reaction mixture was heated under reflux for 20 h, and then worked-up in a similar manner as above to yield colorless crystals of the tetramethylammonium salt of the borate **5** (0.87 g, 47% yield), which melted with decomposition at 88 °C (from dichloromethane–hexane). ^{1}H NMR (CD_3OD): δ = 7.70–7.40 (m, arom., 12H), 3.84 (q, J = 8 Hz, OCH_2CF_3, 8H) and 3.21 ppm (s, $N(CH_3)_4$, 12H); ^{19}F NMR (CD_3OD): δ = 100.8 (s, Ar–CF_3, 12F), 92.8 (s, $C(CF_3)_2OCH_2$, 24F), and 89.1 (t, J = 8 Hz, OCH_2CF_3, 12F); $\lambda_{max}(\varepsilon)$ (CH_2Cl_2): 281 (4.1×10^3) and 272 nm (4.6×10^3). Analysis: Found: C, 37.42; H, 1.89, N, 1.17%. Calcd. for $C_{52}H_{32}NO_4BF_{48}$: C, 37.68; H, 1.95; N, 0.85%.

Measurement of solubility of tetraarylborates

A relationship between the concentration and absorbance at absorption maximum was determined with dichloromethane solutions of a range of known concentrations of each tetraarylborate. Values of the molar extinction coefficients in dichloromethane were calculated from the slopes of these linear plots, as shown in Table 3.

The concentration of a solution saturated with a tetraarylborate salt in dichloromethane was determined spectrophotometrically after the solu-

TABLE 3

Values of molar extinction coefficients at absorption maximum

Borate compd	$\varepsilon(\lambda_{max}(nm))$
TFPB (**1**), $R_1 = R_2 = CF_3$	4700 (270)
3, $R_1 = R_2 = C(CF_3)_2OCH_3$	5450 (273)
4, $R_1 = C(CF_3)_2OCH_3$, $R_2 = CF_3$	5200 (272)
5, $R_1 = C(CF_3)_2OCH_2CF_3$, $R_2 = CF_3$	4600 (272)

tion was diluted with dichloromethane. Those of saturated solutions in other solvents were determined as follows. An aliquot of the saturated solution was evaporated off and the residue was then dissolved in dichloromethane. The concentration of the original saturated solution was calculated from the spectrophotometric measurement of the dichloromethane solution.

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