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Promising route to aryl(polyfluoroorganyl)borates: aryltris(pentafluorophenyl)borates

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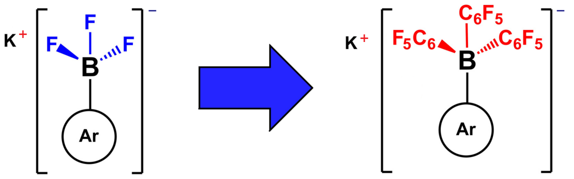
Simple preparation of potassium aryltris(pentafluorophenyl)borates by nucleophilic perfluoroarylation of potassium aryltrifluoroborates with C_6F_5MgBr is offered.



Ar = Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-FC_6H_4, 4-$F_3CC_6H_4$, C_6F_5, β-$C_{10}F_7$

Keywords: organofluoroborate anions, polyfluoroarylborates, nucleophilic perfluoroarylation, organofluorine compounds, organoboron compounds.

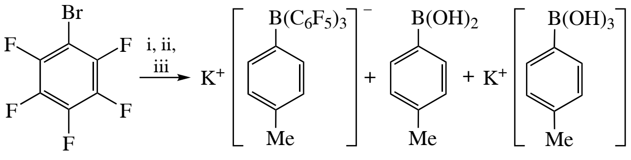
Salts of tetrakis(perfluoroaryl)borates are thermally and chemically resisted compounds[1–3] which find use in polymerization of olefins (co-catalysts),[4–7] photopolymerization (photoacid generators)[8–10] and electrochemical processes,[11,12] and serve as counteranions for labile positively charged systems,[13] ionic liquids,[14] *etc*. In the course of our systematic investigation on polyfluorinated organoboron compounds we needed a general route to non-symmetric aryl(polyfluoroaryl)-borates of type $M[ArB(Ar^F)_3]$. The known methods are based on the nucleophilic addition of polyfluoroaryllithium (polyfluoroarylmagnesium bromide) Ar^FM (poor nucleophiles) to aryldihaloboranes $ArBX_2$ (strong electrophiles)[15,16] or ArM (strong nucleophiles) to tris(polyfluoroaryl)borane (strong electrophiles).[17–19] The first approach deals with the preliminary preparation of moisture-sensitive aryldihaloboranes whereas the second route requires the pre-synthesis of tris(polyfluoroaryl)-borane. Tris(pentafluorophenyl)borane is the only commercially available substrate and it is expensive. Synthesis and, especially, purification of tris(polyfluoroaryl)boranes is hard and labor-intensive process.[20,21]

We elaborated more convenient procedure for the preparation of the abovementioned non-symmetric borates $M[ArB(Ar^F)_3]$ by reaction of (polyfluoroaryl)magnesium bromide with easily available potassium aryltrifluoroborates. In this communication, the synthesis of aryltris(pentafluorophenyl)borates as the first series of this family is presented. Preliminary experiments using the reaction of C_6F_5MgBr with $K[4\text{-}MeC_6H_4BF_3]$ **1** really afforded the desired borate $K[4\text{-}MeC_6H_4B(C_6F_5)_3]$ **2**, however, despite the excess of the nucleophile by-products **3** and **4** were also formed (Scheme 1). Since the actual reactive species is aryldifluoroborane formed in the course of dissociation of **1**, the presence of **3** and **4** is a consequence of hydrodeboration of unreacted $K[4\text{-}MeC_6H_4BF_3]$.[22]

Our efforts to optimize the reaction conditions (see Online Supplementary Materials) showed that the yield of **2** depended on the order of mixing of the reactants, the temperature, and the duration of the process. When solid borate **1** was added to ethereal solution of C_6F_5MgBr (direct order) and the reaction mixture was stirred at room temperature or refluxed, the desired borate **2** was obtained in negligible yield, while **3**, **4** and unreacted **1** were the main products. We suppose that this occurred due to negative effect of unreacted magnesium metal, similar to what was observed previously.[23] The best result was achieved by slow addition of C_6F_5MgBr in diethyl ether to a suspension of **1** in diethyl ether at 7–10 °C (reverse order) followed by continuous reflux. In this case, only traces of **3** and **4** were detected. Likely, the long duration of the reaction is due to the increase in steric hindrance at the boron atom when the fluorine atoms are replaced by bulky C_6F_5 groups. In parallel way, the fluoride donating ability of the formed borates $[ArB(C_6F_5)_nF_{3-n}]^-$ ($n = 1, 2$) should diminish because the Lewis acidity of the corresponding boranes increases.

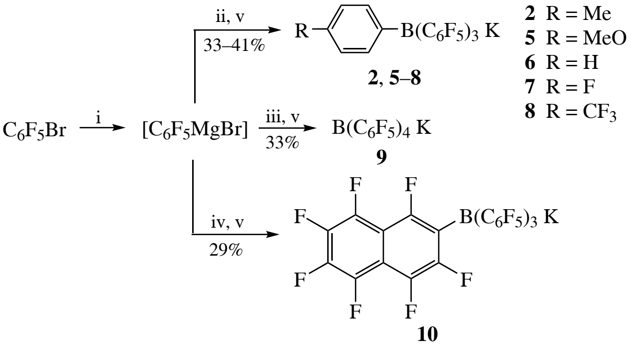
Based on these results, pentafluorophenylation of a series of potassium aryltrifluoroborates was carried out (Scheme 2). Despite the increase in Lewis acidity of the conjugated aryldifluoroboranes[†] and, as a consequence, a decrease in their equilibrium concentration, the target non-symmetric aryltris(pentafluorophenyl)borates **2**, **5–10** were obtained in reasonable yields.[‡]

To summarize, using the model reaction between readily available C_6F_5MgBr and $K[ArBF_3]$ we have developed a



2 **3** **4**

Scheme 1 *Reagents and conditions*: i, Mg (1.1 equiv.), BuBr (0.2 equiv.), Et_2O; ii, $K[4\text{-}MeC_6H_4BF_3]$ **1** (0.25 equiv.); iii, K_2CO_3 (sat. aq.).



Scheme 2 *Reagents and conditions*: i, Mg, BuBr, Et_2O, 0–5 °C; ii, $K[4\text{-}RC_6H_4BF_3]$ (0.25 equiv.), Et_2O, <10 °C, then reflux, 12–15 h; iii, $C_6F_5BF_3K$ (0.25 equiv.), Et_2O, <10 °C, then reflux, 18 h; iv, $\beta\text{-}C_{10}F_7BF_3K$ (0.25 equiv.), Et_2O, <10 °C, then reflux, 18 h; v, aq. K_2CO_3.

convenient procedure for the preparation of non-symmetric aryltris(pentafluorophenyl)borates. We anticipate on extending this procedure toward other polyfluoroarylmagnesium reactants.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7575.

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[†] The Lewis acidity increases in the following order: 72.6 ($Ar = C_6H_5$), 75.3 ($Ar = 4\text{-}F_3CC_6H_4$), 76.3 ($Ar = 4\text{-}FC_6H_4$), 79.8 ($Ar = C_6F_5$) and 80.2 ($Ar = \beta\text{-}C_{10}F_7$).[24]

[‡] *Preparation of potassium aryltris(pentafluorophenyl)borates (general procedure).* A 50 ml three-necked flask equipped with magnetic stirring bar, thermometer, dropping funnel and reflux condenser topped with T-adapter for argon inlet/outlet was charged with magnesium (219 mg, 9.0 mmol), several crystals of iodine and was filled with argon. At room temperature, a solution of BuBr (0.17 ml, 1.6 mmol) in diethyl ether (20 ml) was added, and the mixture was stirred till discoloration. The reactor was cooled in an ice bath, and a solution of bromopentafluorobenzene (1.0 ml, 8.0 mmol) in diethyl ether (15 ml) was added dropwise keeping temperature below 10 °C. The reaction mixture was stirred with ice cooling for additional 4.5 h. Another 100 ml three-necked flask equipped with magnetic stirring bar, thermometer and reflux condenser topped with T-adapter for argon inlet/outlet was charged with potassium aryltrifluoroborate (2.0 mmol) and filled with argon. After addition of diethyl ether (20 ml), the suspension was cooled in an ice bath, and cold solution of C_6F_5MgBr was siphoned from the first flask under argon to keep temperature at 7–10 °C. The reaction mixture was warmed to room temperature and then refluxed for 12–18 h. After cooling to room temperature, the mixture was poured into a saturated solution of potassium carbonate (10 ml), and the suspension was filtered. The organic phase was separated, the aqueous one was extracted with diethyl ether (2 × 10 ml), and the filter cake was washed with diethyl ether (2 × 15 ml). The combined extract was dried with $MgSO_4$ and the solvent was removed on evaporator. The residue was dissolved in hot water (25 ml) and boiled with active charcoal (1–1.5 g) for 20–30 min. After filtration, the aqueous solution was evaporated under reduced pressure to yield white or pale yellow solid.

It is of note that the ^{19}F NMR spectrum of sterically hindered borate **10** contains signals for three C_6F_5 groups, distinguished from each other: six resonances of F-*ortho*, and three resonances of F-*para*, while resonances of F-*meta* remain equal.