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The first example of the *ortho*-directing effect of the weakly coordinating substituent [–BF$_3$]$^-$ in the catalytic hydrodefluorination of the pentafluorophenyltrifluoroborate anion

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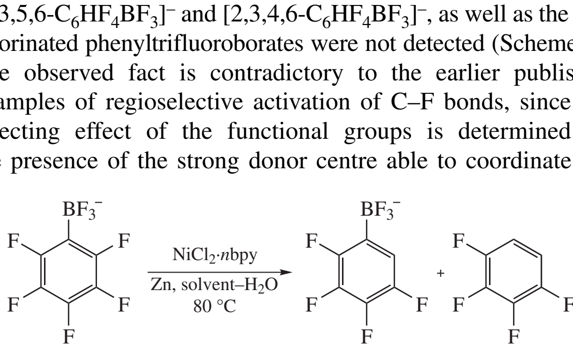
The pentafluorophenyltrifluoroborate anion undergoes hydrodefluorination under the action of zinc in the presence of nickel complexes turning into the 2,3,4,5-tetrafluoroborate anion.

The highly regioselective activation of aromatic carbon–fluorine bonds by transition metal complexes is of theoretical and practical interest.[1] Polyfluorinated azobenzenes, $C_6F_5N{=}NC_6X_5$ (X = H, F), undergo *ortho*-metaldefluorination (fluorine substitution by metal atom) with $Mn_2(CO)_{10}$[2] and $CpRu(PPh_3)_2Me$.[3] 'Ligand assistance' of Schiff bases derived from C_6F_5CHO and some 1,2-diamines occurs in reactions of oxidative addition of W, Mo, Ni[4] and Pt[5] complexes. Similar effects were observed for other fluorinated aromatic compounds forming complexes with palladium,[6] platinum[7] and iridium.[8] Intramolecular dehydrofluorinative coupling takes place in the case of Rh and Ir.[9] Pentafluoropyridine and 2,3,5,6-tetrafluoropyridine react with $Ni(COD)_2$ and PEt_3 in hexane to give predominantly [(2-polyfluoropyridyl)Ni$(PEt_3)_2$F] complexes.[10] Selective *ortho*-hydrodefluorination occurs in C_6F_5COOH after treatment with $Yb(C_6F_5)_2$[11] and $YbCp_2(dme)$.[12] In the last case, it proceeds in a catalytic way.

Earlier, we reported the highly regioselective catalytic activation of aromatic C–F bonds in derivatives of pentafluorobenzoic acid C_6F_5COX (X = OH, NH_2, OEt)[13] and pentafluoroaniline C_6F_5NHY (Y = COMe),[14] proceeding in the presence of nickel complexes under reductive conditions. In this work, we observed that pentafluorophenyltrifluoroborate anion $[C_6F_5BF_3]^-$ **1** introduced in the reaction as a potassium salt also reacts with zinc in the presence of $NiCl_2{\cdot}n$bpy under the described conditions.[13,14] The expected reaction route is the formation of an isomeric mixture of $[C_6F_4HBF_3]^-$ anions. Surprisingly, the actual reaction product is a salt of 2,3,4,5-tetrafluorophenyltrifluoroborate anion, [2,3,4,5-$C_6HF_4BF_3$]$^-$ **2**. The isomers [2,3,5,6-$C_6HF_4BF_3$]$^-$ and [2,3,4,6-$C_6HF_4BF_3$]$^-$, as well as the less fluorinated phenyltrifluoroborates were not detected (Scheme 1). The observed fact is contradictory to the earlier published examples of regioselective activation of C–F bonds, since the directing effect of the functional groups is determined by the presence of the strong donor centre able to coordinate the transition metal atom. At the same time, the [–BF$_3$]$^-$ group of $[C_6F_5BF_3]^-$ **1**, by analogy with structurally close anion $[BF_4]^-$, belongs to weakly coordinating anions.[15]



1 **2** **3**

Scheme 1

Table 1 Hydrodefluorination of $[C_6F_5BF_3]^-$ **1** in NMP.

Run	Catalyst (mol%)	LiCl (equiv.)	Composition of the reaction mixture (mol%)		
			1	**2**	**3**
1	$NiCl_2{\cdot}2$bpy (10)[a]	—	96	4	—
2	$NiCl_2{\cdot}2$bpy (10)[b]	—	95	5	—
3	$NiCl_2{\cdot}2$bpy (10)	—	92	8	—
4	$NiCl_2{\cdot}$bpy (10)[c]	—	99	Traces	—
5	$NiCl_2{\cdot}3$bpy (10)[c]	—	83	17	—
6	$NiCl_2{\cdot}3$bpy (20)	—	76	24	—
7	$NiCl_2{\cdot}3$bpy (5)[d]	—	75	25	—
8	$NiCl_2{\cdot}3$bpy (10)[e]	—	78	22	—
9	$NiCl_2{\cdot}3$bpy (10)[f]	—	74	26	—
10	$NiCl_2{\cdot}3$bpy (50)[g]	—	80	20	—
11	$NiCl_2{\cdot}3$bpy (100)[g]	—	62	32	—
12	—	—	100	—	—
13	$NiCl_2{\cdot}3$bpy (10)	5	52	44	8
14	$NiCl_2{\cdot}3$bpy (10)	10	40	32	24
15	$NiCl_2{\cdot}3$bpy (10)	15	20	57	23
16	—	15	95[h]	—	—
17	$NiCl_2{\cdot}3$bpy (50)	5	—	22	8[i]

[a] DMF was used as solvent. [b] DMA was used as solvent. [c] Duration of 6 h. [d] Zn dust (10 equiv.) was added in 5 portions. [e] Zn dust (20 equiv.) was added in one portion. [f] Zn dust (20 equiv.) was added in 5 portions; [g] Zn dust (10 equiv.) was added in one portion. [h] C_6F_5H (5 mol%) was detected. [i] Additionally, 1,2,3-$C_6F_3H_3$ (33 mol%) and 1,2-$C_6F_2H_4$ (37 mol%) were detected.

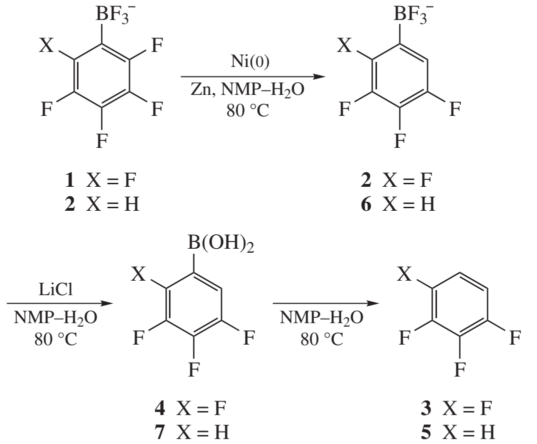
The catalyst was prepared *in situ* from nickel chloride and a necessary amount of 2,2′-bipyridine. The reaction was carried out at 80 °C.[†] The reaction mixtures were analyzed by ^{19}F NMR

[†] *General procedure of the hydrodeboration.* A flask supplied with a magnetic stirrer bar and heating bath was charged with $NiCl_2{\cdot}6H_2O$ (10 mol%: 6 mg, 0.025 mmol), the respective amounts of 2,2′-bipyridine ($NiCl_2{\cdot}$bpy: 3.9 mg, 0.025 mmol; $NiCl_2{\cdot}2$bpy: 7.8 mg, 0.050 mmol; $NiCl_2{\cdot}3$bpy: 11.7 mg, 0.075 mmol), 1 ml of the solvent (DMF, DMA or NMP) and 0.2 ml of water. The reaction mixture was stirred at 80 °C for 1 h, then 163.5 mg (2.5 mmol) of zinc dust were added in one portion. After stirring for 10 min, 69 mg (0.25 mmol) of K[$C_6F_5BF_3$] were added. The resulting reaction mixture was stirred at 80 °C for 8 h and cooled down to ambient temperature. A quantitative internal standard ($C_6H_5CF_3$) was added, and the mixture was analyzed by ^{19}F NMR spectroscopy (282.4 MHz).

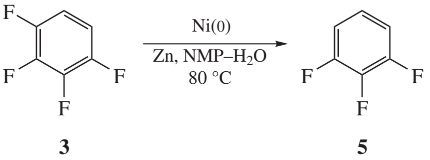
spectroscopy (Table 1). Conversion of 4–8% of anion **1** was achieved in the presence of $NiCl_2 \cdot 2bpy$ for 8 h and anion **2** was the only product of the reaction (Table 1, runs 1–3). The anion $[2,3,4,5\text{-}C_6HF_4BF_3]^-$ **2** possesses five signals in the ^{19}F NMR spectrum attributed to four aromatic fluorine and $[-BF_3]^-$ group[‡] whose chemical shifts and multiplicities agree with those for an authentic sample and earlier described salt $K[2,3,4,5\text{-}C_6HF_4BF_3]$.[16]

The course of the hydrodefluorination depends on the nature of the solvent used as the reaction medium. Among a series of aprotic dipolar solvents, such as DMF, DMA and NMP, the most appropriate is the latter (Table 1, run 3). The nature of the catalytic complex is another factor, which determines the conversion of starting compound **1** in analogy to pentafluoroacetanilide.[14] For instance, no transformations of **1** were detected in the presence of $NiCl_2 \cdot 1bpy$ (10 mol%) and Zn (in excess) (Table 1, run 4). At the same time, the increase in a number of the ligands up to 3 relatively to nickel leads to a remarkable rise of the catalytic activity of the nickel complex (Table 1, run 5). Nevertheless, the maximum conversion of 24% was achieved only when 20 mol% of the catalyst was applied (Table 1, run 6). All efforts to raise the reactivity of **1** by means of the increase of the amount of zinc or change of the order of its addition allowed to rise the conversion of $[C_6F_5BF_3]^-$ only up to 25% (Table 1, runs 7–10). Surprisingly, the complete conversion of anion **1** was not obtained even in the presence of 100 mol% of nickel complex (Table 1, run 11). In the absence of a catalyst, $[C_6F_5BF_3]^-$ does not react with Zn in aqueous NMP (Table 1, run 12).

During investigation of impact of different additives on the conversion of anion **1**, we observed that the reactivity of **1** increases substantially in the presence of lithium chloride (Table 1, runs 13–15). However, in runs 13–15, we disclosed the formation of 1,2,3,4-tetrafluorobenzene **3**[§] along with anion **2** (Scheme 1). Probably, benzene **3** is a product of transformations of anion **2** into the corresponding fluorinated phenylboronic acid **4** under the action of the lithium salts[17] with subsequent hydrodeboration of the latter (Scheme 2).[18] Initial anion **1** also slowly reacts with LiCl to give pentafluorobenzene, being the hydrodeboration product of pentafluorophenylboronic acid (Table 1, run 16).[18] The increase in the LiCl and catalyst concentration leads to consumption of the initial compound. However, significant amounts of 1,2,3-trifluorobenzene **5**[¶] were observed along with $[2,3,4,5\text{-}C_6HF_4BF_3]^-$ **2** and 1,2,3,4-tetrafluorobenzene **3** (Table 1, runs 14, 15 and 17). There are two main pathways for the formation of fluorobenzene **5**. Compound **5** can be a product of tetrafluorobenzene **3** hydrodeboration (Scheme 3).[19] The other way includes a stepwise transformation of anion **2** into $[3,4,5\text{-}C_6H_2F_3BF_3]^-$ **6** followed by its transformation into 3,4,5-trifluorophenylboronic acid **7** and hydrodeboration of the latter (Scheme 2).



Scheme 2



Scheme 3

Thus, we observed the first example of *ortho*-directing effect of a weakly coordinating substituent $[-BF_3]^-$ in the transition metal catalysed hydrodefluorination of the polyfluoroaryltrifluoroborate anion. We can assume that the most plausible reason of the *ortho*-directing effect is the interaction of the Ni atom with the negatively charged fluorine atom bonded to boron.

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[‡] Structure of anion $[C_6F_5BF_3]^-$ was proved by ^{19}F NMR spectroscopy (NMP) δ: −135.59 (m, 2-F, ${}^3J_{FF}$ 20 Hz, ${}^5J_{FF}$ 15 Hz), −139.36 (q, BF_3, ${}^1J_{BF}$ 45 Hz), −143.31 (m, 5-F, ${}^3J_{FF}$ 19.7 Hz), −160.05 (m, 3-F, ${}^3J_{FF}$ 20 Hz, ${}^3J_{FF}$ 20 Hz), −162.69 (m, 4-F, ${}^3J_{FF}$ 19 Hz, ${}^4J_{FF}$ 9 Hz) [lit.,[16] (CD_3CN) δ: −135.25 (m, 2-F, ${}^3J_{FF}$ 22 Hz, ${}^4J_{FF}$ 9 Hz), −139.16 (m, BF_3), −143.01 (m, 5-F, ${}^3J_{FF}$ 19 Hz), −159.72 (m, 3-F, ${}^3J_{FF}$ 19 Hz, ${}^3J_{FF}$ 22 Hz), −162.04 (m, 4-F, ${}^3J_{FF}$ 19 Hz)].

[§] *1,2,3,4-Tetrafluorobenzene*: ^{19}F NMR (NMP) δ: −139.93 (m, 2F, 1,4-F, ${}^3J_{FF}$ 18 Hz, ${}^3J_{HF}$ 7 Hz), −157.07 (m, 2F, 2,3-F, ${}^3J_{FF}$ 18 Hz, ${}^3J_{FF}$ 19 Hz, ${}^4J_{HF}$ 5 Hz) [lit.,[20] δ: −139.8 (m, 2F; 1,4-F), −156.8 (m, 2F, 2,3-F)].

[¶] *1,2,3-Trifluorobenzene*: ^{19}F NMR (NMP) δ: −135.85 (m, 2F, 1,3-F, ${}^3J_{FF}$ 21 Hz, ${}^3J_{HF}$ 8 Hz), −162.45 (m, 1F, 2-F, ${}^3J_{FF}$ 21 Hz, ${}^4J_{HF}$ 6 Hz) [lit.,[20] δ: −136.2 (m, 2F, 1,3-F), −163.0 (m, 1F, 2-F)].

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