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# Hydrogenolysis of C–F bonds in fluorinated aromatic hydrocarbons catalysed by nickel complexes

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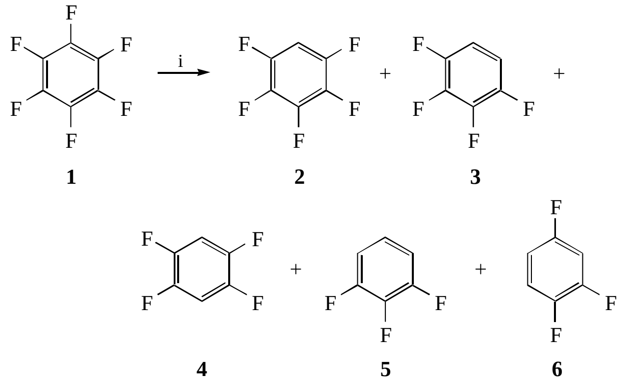
**Reactions of hexafluorobenzene, pentafluorobenzene, octafluoronaphthalene and pentafluoropyridine with the $NiCl_2$–2,2′-bipyridine (or 1,10-phenanthroline)–Zn reductive catalytic system in DMF (or DMA) in the presence of water or ammonium chloride resulted in the products of C–F bond hydrogenolysis.**

The activation of C–F bonds by transition metal complexes is an urgent problem.[1,2] However, only a few of examples of the catalytic activation of C–F bonds are known. Aizenberg and Milstein[3] reported on the hydrodefluorination of hexafluorobenzene **1** and pentafluorobenzene **2** under catalysis with trimethylphosphine complexes of rhodium. Kiplinger and Richmond[4] found that the interaction of fluorinated aromatic compounds with the $Cp_2MX_2$–$HgCl_2$–Mg and $Cp_2MX_2$–$PMe_3$–Mg reductive systems (M = Ti or Zr; X = Cl or F) results in the hydrogenolysis of aromatic C–F bonds. Deacon *et al.*[5] suggested a procedure for the synthesis of 2,3,4,5-tetrafluorobenzoic acid by defluorination of pentafluorobenzoic acid in the presence of an $YbCp_2$(dme) catalyst.

We found that the hydrogenolysis of aromatic C–F bonds in polyfluoroaromatic compounds easily proceeds under the action of the $NiCl_2$–2,2′-bipyridine (bipy) [or 1,10-phenanthroline (phen)]–Zn reductive system in DMF or DMA in the presence of $H_2O$ or $NH_4Cl$.[†] No reaction was observed in the absence of $H_2O$ or $NH_4Cl$. The same result was achieved without the $NiCl_2$–bipy (or phen) catalytic complex.

The reduction of hexafluorobenzene **1** for 3 h resulted in the complete conversion into pentafluorobenzene **2**, 1,2,3,4- and 1,2,4,5-tetrafluorobenzenes **3** and **4**, 1,2,3- and 1,2,4-trifluorobenzenes **5** and **6**, which were isolated in 19, 52, 14, 5 and 2% yields, respectively.

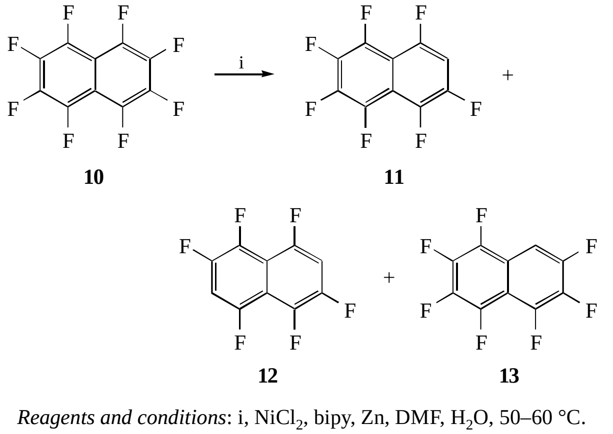


*Reagents and conditions*: i, $NiCl_2$, bipy, Zn, DMA, $NH_4Cl$, 70 °C, 3 h.

Note that the yield of 1,2,3,4-tetrafluorobenzene **3** was higher than that of 1,2,4,5-tetrafluorobenzene **4** by a factor of about four, and 1,2,3,5-tetrafluorobenzene **7** was absent. The replacement of bipy with phen in the catalytic complex exerted almost no effect on the reaction. The use of DMF as a solvent, resulted in a decrease in the conversion of **1** (to 62% in 5 h). In this case, pentafluorobenzene **2** was the main product of the reaction, and compounds **3** and **4** were formed in minor amounts. In the presence of $NH_4Cl$ as a source of protons, the effective amount of a reducing agent (zinc) was 6 equiv. per 1 equiv. of the substrate, whereas about 10 equiv. of zinc per 1 equiv. of the substrate were required with the use of water. The latter reduction system was as good as that with ammonium chloride, and reproducibility of the results was better. For this reason, the reduction of other polyfluoroaromatic compounds was studied with the use of the $NiCl_2$–bipy–Zn reduction system in aqueous DMF.

The reaction of **2** with the $NiCl_2$–bipy–Zn reduction system at 100% conversion (4 h) gave a mixture of fluorinated benzenes **3**–**6** in 45, 11, 18 and 15% yields, respectively. In addition, 1,2- and 1,4-difluorobenzenes **8** and **9** (*ca.* 1%) were formed. In this case, the ratio between isomers **3** and **4** was practically the same as in the case of hexafluorobenzene; 1,2,3,5-tetrafluorobenzene **7** was also not detected. For comparison, note that the reduction of **2** with lithium aluminium hydride gave 1,2,4,5-tetrafluorobenzene **4** (92%) with impurities of 1,2,3,4-tetrafluorobenzene **3** (7%) and 1,2,3,5-tetrafluorobenzene **7** (1%).[6] The reactions of **1** and **2** with titanium, zirconium[4] and rhodium[3] complexes resulted only in compound **4**. Of three possible isomers, only the formation of 1,2,4,5-tetrafluorobenzene **4** was observed in the reaction between pentafluorobenzene and tetrakis(triethylphosphine)nickel(0).[7] Note that the catalytic activity of nickel complexes with phen is almost the same as that of $NiCl_2$–bipy complexes.

The reduction of octafluoronaphthalene **10** by the $NiCl_2$–bipy–Zn system in aqueous DMF at 60 °C afforded polyfluorinated naphthalenes **11**–**13**.



*Reagents and conditions*: i, $NiCl_2$, bipy, Zn, DMF, $H_2O$, 50–60 °C.

At low conversion (10–15 %) of substrate **10**, the main product was 1,2,3,4,5,6,8-heptafluoronaphthalene **11**. At 70% conversion of **10** (2 h), in addition to **11** (70%), 1,2,4,5,6,8-hexafluoronaphthalene **12** (25%), 1,2,3,4,5,6,7-heptafluoronaphthalene **13**

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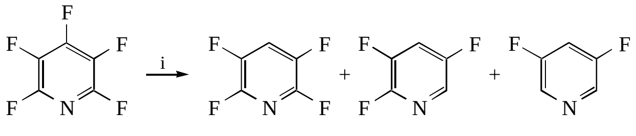
[†] *General procedure*: $NiCl_2\cdot 6H_2O$ (0.12 g, 0.5 mmol), 0.08–0.16 g (0.5–1 mmol) of bipy [or 0.1–0.2 g (0.5–1 mmol) phen] and zinc dust (6.5 g, 100 mmol) were placed in a flask. Next, DMF (or DMA) (10 ml) and $H_2O$ (2 ml) (or 1 g of ammonium chloride) were added, and the mixture was heated at 70 °C for 30 min with stirring. A substrate (10 mmol) solution in DMF or DMA (5 ml) was added dropwise, and the resulting reaction mixture was stirred for several hours (see the text). The reaction was monitored by reversed-phase HPLC (eluent: aqueous acetonitrile; UV detection at 230 and 254 nm). Next, the solution was filtered and diluted with water, and the products were stream distilled. The products were analysed by $^{19}F$ NMR spectroscopy and GC–MS. The identification of compounds was made by comparison of the retention times and mass spectra with those for standard samples.

(*ca*. 5%) and unidentified fluoronaphthalenes (*ca.* less 1%) were formed. The further reaction led to the complete conversion of **10** into a complex mixture of fluorine-containing naphthalenes. Note that the interaction of octafluoronaphthalene **10** with low-valence titanium and zirconium[4] complexes and with zinc in aqueous ammonia[8] resulted only in compounds **11** and **12**.

The interaction of pentafluoropyridine **14** with $NiCl_2$–bipy–Zn gave 2,3,5,6-tetrafluoropyridine **15**, 2,3,5-trifluoropyridine **16** and 3,5-difluoropyridine **17**.



**14** **15** **16** **17**

*Reagents and conditions*: i, $NiCl_2$, bipy, Zn, DMF, $H_2O$, 60 °C.

Compound **14** was completely consumed within 1 h to give compounds **15**–**17** in 45, 27 and 18% yields, respectively. In contrast to the reaction between compound **14** and lithium aluminium hydride with deep hydrodefluorination,[9] in our case, fluorine atoms were not replaced by hydrogen in 3,5-difluoropyridine **17**. Note that the reduction of pentafluoropyridine with a zinc–copper couple (aqueous DMF, 70 °C, 10 h) gave only tetrafluoropyridine **15**.[10]

Thus, hexafluorobenzene, pentafluorobenzene, octafluoronaphthalene and pentafluoropyridine react with a catalytic system *in situ* generated from nickel chloride, 2,2′-bipyridyl (or 1,10-phenanthroline) and zinc in DMF (or DMA) in the presence of water or ammonium chloride to form hydrodefluorination products resulting from the hydrogenolysis of aromatic C–F bonds.

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